A Thesis

Entitled

"THE CRYSTAL STRUCTURES OF SOME ACID SALTS AND RELATED COMPOUNDS."

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by

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PREFACE.

I wish to express my thanks to Dr. J.C. Speakman for advice and direction throughout this period of research. I should also like to thank Professor J. Monteath Robertson for his interest.

The extensive calculations were performed on the Glasgow University DEUCE computer. I am indebted to those authors who made their programs for DEUCE available to me, in particular to Dr. J.S. Rollett and Dr. J.G. Sime.

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C O N T E N T S.

SUMMARY.

This thesis describes a study of the crystal structures of some organic salts by X-ray methods. The thesis is divided into three chapters. Chapter One consists of a review of the theoretical principles underlying the elucidation and refinement of structures.

Chapter Two, which is in five sections, is concerned with the crystal structures of the acid salts of some monobasic carboxylic acids. The interesting structural feature of these acid salts lies in the hydrogen bonding involved and, in the first section, this is discussed. The second section consists of a refinement of the structure of sodium hydrogen diacetate by the method of least-squares. Coordinates are assigned to the hydrogen atoms of the methyl group. In section three, a three-dimensional refinement of ammonium hydrogen dicinnamate by Fourier and least-squares methods is described. Section four contains a study of the isomorphous rubidium, potassium and ammonium acid salts of p-chlorobenzoic acid. The structure is solved by two-dimensional methods. Some three-dimensional data for the potassium salt, which have been corrected for absorption, are used in a

least-squares refinement of the structure. Each section is concluded with a discussion of the significance of the structure and molecular geometry obtained. In particular, these acid salts have structures in which the acidic groups are equivalent and are joined by a short hydrogen bond which is crystallographically symmetrical. This aspect is considered in the final section.

Chapter Three is devoted to a study of the basic salt, N-α-picoline oxide hemihydrobromide. This salt is the basic analogue of the acid salts described in Chapter Two. The space group is C2/c and the structure is found by solving the Patterson projections along the b-axis and the C- face diagonal. For the interpretation of this latter projection, the lattice is described in terms of a primitive triclinic sub-cell. The two projections are used to give the three-dimensional structure referred to the monoclinic cell. The interesting feature of the structure is the presence of a short symmetrical hydrogen bond between the oxygen atoms of two N-α-picoline oxide molecules similar to the type observed in the acid salts.

CHAPTER I.

A REVIEW OF SOME X-RAY DIFFRACTION METHODS.

1.1. Introduction.

In 1912, Von Laue obtained diffraction effects by passing X-rays, whose nature at this time was in doubt, through a crystal. This established the wave nature of X-rays and eventually led to discoveries which had a profound effect on the structure of the atom. It also proved, conclusively, the periodic distribution of matter in crystals, a theory which had been held for over two centuries.

Soon after Laue's observation, it was realised that the diffracted X-ray beams could be used to give the image of the object causing the scattering, viz., the atomic arrangement. Mathematical methods have been developed which relate the intensity of the diffracted beam to the crystal structure and these are reviewed in the course of this chapter.

Unfortunately, part of the information required to give a representation of the atoms in a crystal is lost when the experiment of recording the intensities of the diffracted beam is made and the problem of overcoming this difficulty is the barrier to the solution of crystal structures as a matter of routine. Once this problem has been solved, it is possible, in principle, to obtain the absolute position in space of every atom.

As well as this fundamental difficulty, there is the practical difficulty of the immense calculations which have to be performed in the course of an analysis. Before the advent of high-speed computing facilities, this factor severely limited the size of the molecule studied and the degrees of accuracy and completeness achieved.

To-day the results from X-ray analyses can be divided into two categories. First, they can provide a complete picture of hitherto unknown complex molecules such as naturally occurring organic compounds and proteins. Secondly, they can be used to give bond lengths and bond angles in the molecule under study and, also, distances between atoms in neighbouring molecules. Such results are essential if advances are to be made in the theory of chemical bonding. This thesis is concerned with results of the second category and is a quantitative study of organic compounds whose molecular constitutions are well-known but whose moledular dimensions and intermolecular bonding are of considerable interest.

1.2. Diffraction by a three-dimensional lattice.

As a crystal consists of a repetitive three-dimensional array of atoms, molecules or ions, there must be some unit of structure which, on being repeated, produces the crystal.

If an arbitrary origin is defined, then it will be possible to find further points in space which have an environment identical to that of the origin. These points define a lattice which can be described in terms of three non-coplanar vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$. These vectors contain a volume which is called the unit cell.

The lattice is important as it decides completely the conditions for diffraction. The relationship between the crystal lattice and the scattered radiation is expressed in Bragg's Law or, more generally, in terms of the reciprocal lattice. It is unnecessary to consider the finer details of the structure.

It is assumed that each point of the lattice scatters identically and let A and B in Fig.I be two such points specified by the vector $\underline{r}$ such that:-

$$\underline{r} = x\underline{a} + y\underline{b} + z\underline{c} ,$$

where x, y and z are integers.

A beam of X-rays is now allowed to fall on the lattice and be scattered by each point of the lattice. Let the incident beam be defined by the vector $\underline{s}_o$ and the unit vector in direction $\underline{s}_o$, which is defined as $\frac{\underline{s}_o}{|\underline{s}_o|}$, be $\lambda\ \underline{s}_o$.

It is necessary to consider the phase difference in some direction defined by the vector $\underline{s}$ between the waves

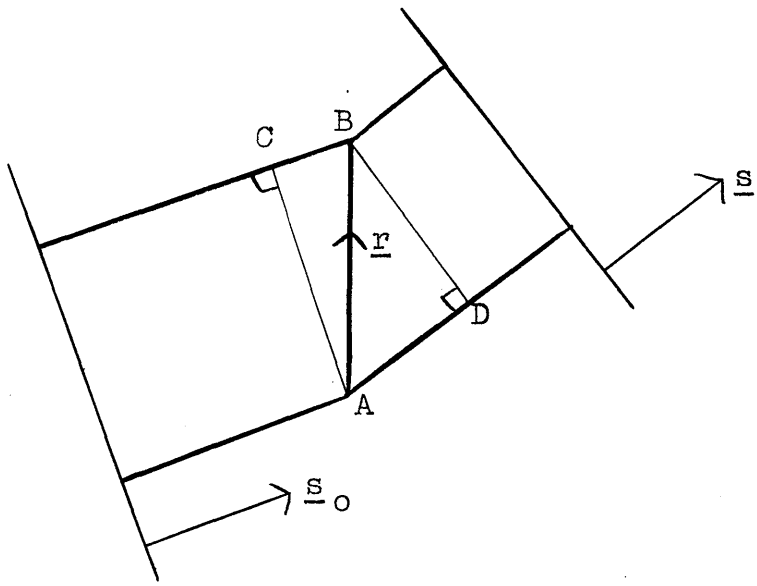


Fig.I.

scattered by any two lattice points such as A and B. The magnitude of the unit vector in the direction $\underline{s}$ is the same as that in the direction $\underline{s}_o$. The phase of a given wave at any point is proportional to the distance from that point to the origin and, hence, the phase difference, ψ, between the waves scattered in the given direction from A and B is

$$\begin{aligned} \psi &= AD - CB \\ &= \text{Proj}^{n.} \text{ of } \underline{r} \text{ on } \underline{s} - \text{Proj}^{n.} \text{ of } \underline{r} \text{ on } \underline{s}_o \\ &= \lambda(\underline{r}.\underline{s} - \underline{r}.\underline{s}_o) \\ &= \lambda \underline{r}.\underline{R} , \qquad \text{where } \underline{R} = \underline{s} - \underline{s}_o . \end{aligned}$$

It is known that diffraction will take place only when $\psi = m(2\pi)$, where m is integral. If the wavelength is λ, this condition means that the phase difference from the two points must be $m\lambda$;

$$\text{i.e.} \quad \lambda\, \underline{r}.\underline{R} = m\lambda,$$

$$\underline{r}.\underline{R} = m,$$

$$(x\underline{a} + y\underline{b} + z\underline{c}).\underline{R} = m,$$

$$\text{i.e.} \quad \underline{a}.\underline{R} = h$$

$$\underline{b}.\underline{R} = k$$

$$\underline{c}.\underline{R} = \ell,$$

where h, k and ℓ are integral. These equations are known as Laue's equations.

Thus the condition for diffraction is that the scalar products $\underline{a}.\underline{R}$, $\underline{b}.\underline{R}$ and $\underline{c}.\underline{R}$ must be integral.

1.3. Bragg's Law and the Reciprocal Lattice.

The three Laue equations may be rewritten in the form:

$$\underline{a}/h.\underline{R} = 1$$

$$\underline{b}/k.\underline{R} = 1$$

$$\underline{c}/\ell.\underline{R} = 1.$$

From the first two of these equations the following relationship is obtained:

$$\left(\frac{\underline{a}}{h} - \frac{\underline{b}}{k}\right).\underline{R} = 0.$$

i.e. the scalar product of the two finite vectors $\underline{R}$ and $(\underline{a}/h - \underline{b}/k)$ is zero. This occurs only if the two vectors are at right angles; in Fig.II, $\underline{R}$ is perpendicular to PQ.

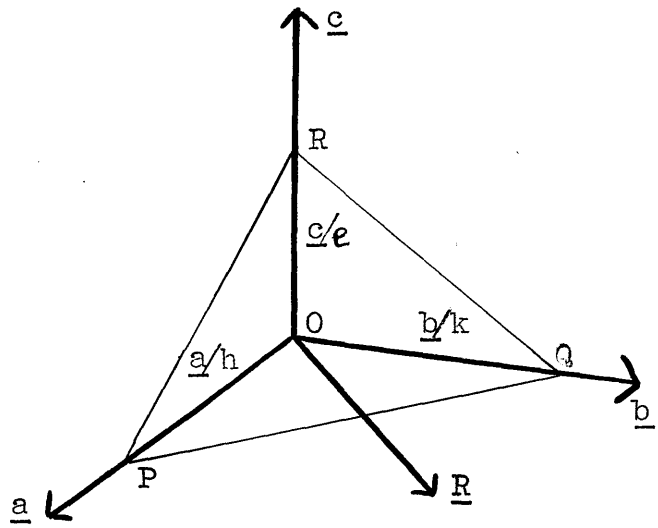


Fig. II.

In a similar fashion it can be shown that $\underline{R}$ is perpendicular to QR and RP in turn. Hence $\underline{R}$ is perpendicular to the plane PQR which has intercepts $(\underline{a}/h, \underline{b}/k, \underline{c}/\ell)$ on the unit cell axis. Thus $\underline{R}$ is in the direction of the normal to plane of Miller indices $(h\,k\,\ell)$.

In Fig.III, let $\underline{s}_o$ make an angle Θ with the plane and,

since $\underline{R}$ must be the bisector of the incident and diffracted beams because $|\underline{s}| = |\underline{s}_o|$, $\underline{s}$ must also be inclined at an angle θ. In this way, the diffraction may be regarded as a reflexion from the plane with Miller indices (h k ℓ).

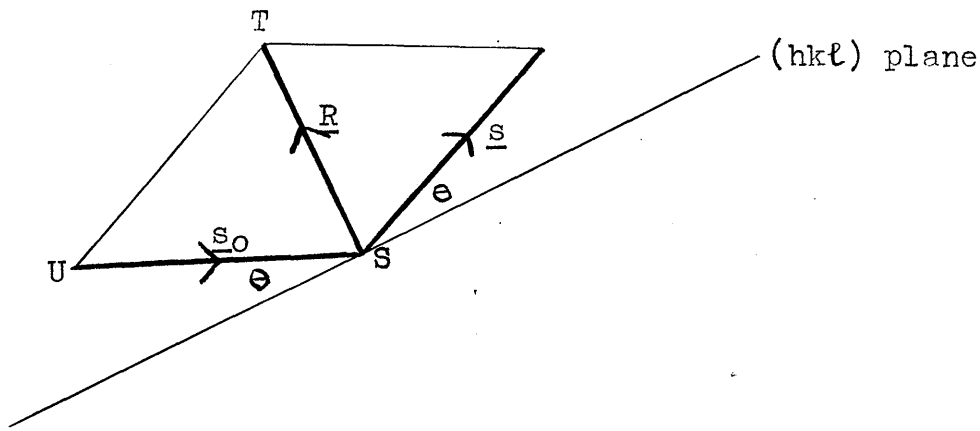


Fig.III.

If US represents the vector $\underline{s}_o$, then

$$|\underline{R}| = ST = 2\,US\cos(90^o-\theta) = 2\sin\theta/\lambda.$$

$$US = |\underline{s}_o| = 1/\lambda.$$

From Fig.II, the distance from the origin to the plane, PQR, d(say), is the projection of the vector $\underline{a}/h$ on the unit vector in the direction of $\underline{R}$.

$$\text{i.e.} \quad d = \underline{a}/h.\ \underline{R}/|\underline{R}|$$

$$= \lambda/2\sin\theta\ ,$$

since $\underline{a}/h.\underline{R} = 1$ by Laue's equations,

$$\text{i.e.} \quad 2\,d\sin\theta = \lambda\ .$$

This equation is known as Bragg's Law.

Alternatively, a solution of the Laue equations may be found in terms of the reciprocal lattice. The vector $\underline{R}$ can be described in terms of three non-coplanar vectors $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$ by the equation,

$$\underline{R} = \xi \underline{a}^* + \eta \underline{b}^* + \zeta \underline{c}^*.$$

The result of substituting this in the Laue equations is

$$\underline{a}.\{\xi \underline{a}^* + \eta \underline{b}^* + \zeta \underline{c}^*\} = h$$
$$\underline{b}.\{\xi \underline{a}^* + \eta \underline{b}^* + \zeta \underline{c}^*\} = k$$
$$\underline{c}.\{\xi \underline{a}^* + \eta \underline{b}^* + \zeta \underline{c}^*\} = \ell.$$

These equations are satisfied only if

$$\xi = h, \quad \eta = k, \quad \zeta = \ell,$$

and $$\underline{a}.\underline{a}^* = \underline{b}.\underline{b}^* = \underline{c}.\underline{c}^* = 1,$$

$$\underline{a}.\underline{b}^* = \underline{a}.\underline{c}^* = \ldots\ldots = \underline{c}.\underline{a}^* = \underline{c}.\underline{b}^* = 0.$$

The two sets of equations can be solved to give

$$\underline{a}^* = \frac{\underline{b} \times \underline{c}}{[\underline{a},\underline{b},\underline{c}]}, \text{ and similar expressions for } \underline{b}^* \text{ and } \underline{c}^*.$$

The lattice defined by the vectors $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$ is known as the reciprocal lattice. Each point on this lattice corresponds to a reflexion from the plane with Miller indices (h k ℓ) and represents the end of the vector which is in the direction of the normal to this plane and has magnitude $1/d(h\ k\ \ell)$.

1.4. The Structure Factor.

In the previous paragraph, the scattering unit was assumed to be an electron positioned at a lattice point. In reality, a crystal consists of a unit, known as the asymmetric unit, of atoms, repeated in three dimensions. In a given direction, the rays scattered by different electrons in the atoms of the asymmetric unit will be out of phase. To find the amplitude and phase of the resultant ray, it is necessary to recombine all the waves.

In Fig.IV, let the origin be at O and let the electron density at some point P be $\rho(x\ y\ z)$ where P is the end of the vector and

$$\underline{r} = x\underline{a} + y\underline{b} + z\underline{c}.$$

x, y and z are now non-integral and are expressed as fractional coordinates of the unit cell edge.

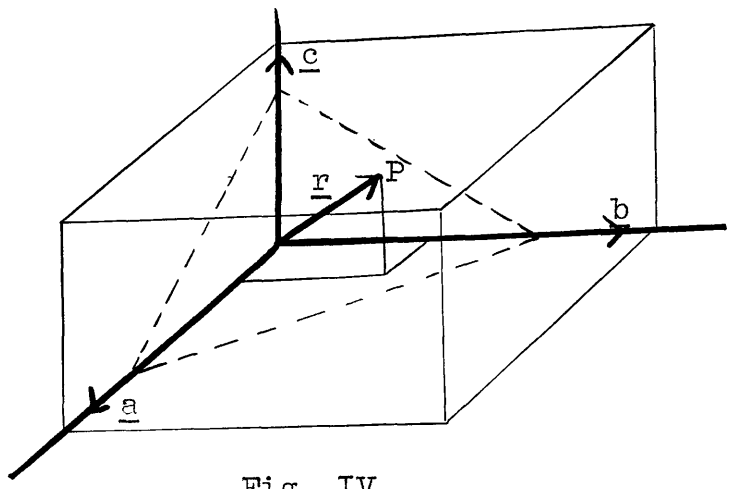


Fig. IV.

The contribution of the electrons in the small volume in the neighbourhood of P will depend on the phase change from O to P. In Fig.IV, the dotted lines define the plane (h k ℓ) and a phase change of 2π corresponds to the perpendicular from the origin to the plane, d(h k ℓ). The phase change of any plane will be proportional to the distance of the plane from the origin. P can be assumed to lie on a plane parallel to (h k ℓ) whose perpendicular distance from the origin will be given by the projection of $\underline{r}$ on the vector describing the normal to the plane (h k ℓ) from the origin. This latter vector has previously been identified with $\underline{R}$ where

$$\underline{R} = h\underline{a}^* + k\underline{b}^* + \ell\underline{c}^*.$$

If φ is the phase of the wave scattered by the element of volume round P, then

$$\begin{aligned} \varphi/2\pi &= \underline{R}.\underline{r} \\ &= \{h\underline{a}^* + k\underline{b}^* + \ell\underline{c}^*\}.\{x\underline{a} + y\underline{b} + z\underline{c}\} \\ &= hx + ky + \ell z. \end{aligned}$$

i.e. $\varphi = 2\pi(hx + ky + \ell z)$.

The contribution from the element of volume is a wave of amplitude $\rho(x\ y\ z)\,\delta V$ and phase φ. As $\rho(x\ y\ z)$ is continuous over the volume of the unit cell, the resultant vector is given by

$$F(hk\ell) = \int_0^1 \rho(xyz) \exp 2\pi i (hx + ky + \ell z)\, dV$$

$$= V \int_0^1\int_0^1\int_0^1 \rho(xyz) \exp 2\pi i (hx + ky + \ell z)\, dx\, dy\, dz.$$

This complex quantity is the structure factor and is the ratio of the amplitude scattered in a certain direction by the contents of the unit cell to the amplitude scattered in the same direction by a single electron.

A more convenient way of evaluating the structure factor is obtained if use is made of the fact that the distribution of electrons about each atom in the structure is known from atomic structure theory. From this known distribution, the scattering factor (f_o) for each atom can be evaluated; it is the ratio of the amplitude scattered by the total number of electrons in the atom (Z, say) in a given direction to the amplitude scattered by a single electron in the same direction. These calculations assume that an atom is spherical symmetrical and that the resultant f_o values are the same in all directions. This means that the effect of bonding on the electrons is ignored. In atoms, electrons have finite volume and phase differences will arise between rays scattered in different parts of the volume . These phase differences are dependent on the value of Θ given in Bragg's equation. If the angle of diffraction is small, i.e. Θ is small, the phase differences are small

and f_o approaches the value Z. As the angle of diffraction increases, the value of f_o falls. The curve of f_o against $\sin\theta/\lambda$ is the scattering factor curve.

The resultant structure factor can be expressed in the form

$$F(hk\ell) = \sum_{j=1}^{J} f_j \exp(i\phi_j),$$

where the summation is taken over the atoms in the unit cell and f_j the scattering factor of the j^{th} atom. The phase angle for each atom, ϕ_j, can be derived in terms of the fractional coordinates (x_j, y_j, z_j) of the mean position of the atom as if the atoms were positioned entirely at (x_j, y_j, z_j).

i.e. $\phi_j = 2\pi(hx_j + ky_j + \ell z_j)$.

The structure factor now becomes

$$F(hk\ell) = \sum_{j=1}^{N} f_j \exp 2\pi i\,(hx_j + ky_j + \ell z_j).$$

$F(hk\ell)$ is a complex quantity and may be expressed in terms of its real and imaginary components,

$$F(hk\ell) = A(hk\ell) + i\,B(hk\ell).$$

Since $\exp i\phi = \cos\phi + i\sin\phi$,

$$F(hk\ell) = \sum_{j=1}^{N} f_j \cos 2\pi(hx_j + ky_j + \ell z_j) + i\sum_{j=1}^{N} f_j \sin 2\pi(hx_j + ky_j + \ell z_j).$$

Equating the real and imaginary parts of the two expressions for $F(hk\ell)$ gives:

$$A = \sum_{j=1}^{N} f_j \cos 2\pi(hx_j + ky_j + \ell z_j),$$

$$B = \sum_{j=1}^{N} f_j \sin 2\pi(hx_j + ky_j + \ell z_j).$$

The modulus of the structure factor, $|F(hk\ell)|$, is called the structure amplitude and is calculated from

$$|F(hk\ell)| = \sqrt{A^2 + B^2}.$$

The phase constant, α, or the argument of the structure factor is evaluated from

$$\alpha(hk\ell) = \tan^{-1} B/A.$$

1.5. Temperature Factor.

At all temperatures, atoms have a finite amplitude of oscillation. This frequency of oscillation (about 10^{13} per second) is much smaller than the frequency of the X-rays (about 10^{18} per second) and the effect could be neglected if only one unit cell were being considered. Since corresponding atoms in the neighbouring unit cells will have this thermal motion but will not be in phase, the scattering produced will tend to interfere. The overall effect can be allowed for empirically if the atomic scattering factors are reduced by an amount which

increases with the diffraction angle, θ . If the atomic scattering factor discussed in the previous section is called f_o and the function to be used in practice is f, then

$$f = f_o \exp(-B \sin^2\theta / \lambda 2)$$

where B is a constant called the temperature factor.

It has been shown (Robertson, 1959) that if the mean square displacement of an atom from a Bragg plane is u^2 and this displacement is isotropic, the value of the constant is given by

$$B = 8\pi^2 u^2 .$$

In general, the thermal displacement will not be isotropic but will be different in different directions and must be described in terms of an ellipsoidal distribution. The following asymmetric temperature factor is assumed to describe this system, (Cruickshank, 1956).

$$\exp -\left[b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + b_{12}hk + b_{23}k\ell + b_{31}h\ell\right]$$

1.6. Fourier Series: Representation of a Crystal.

The electron density of a crystal is periodic in three dimensions and can therefore be represented by a Fourier series.

In general, if the periodic fraction f(x) satisfies

Dirichlet's conditions then f(x) may be expressed as the following series in multiples of φ

$$f(x) = \sum_{n=0}^{\infty} K_n \exp i n \varphi,$$

where the complex numbers, K_n, are the Fourier coefficients.

In this case, the value of φ which corresponds with the Fourier coefficient K(pqr) at some point (x y z) where the electron density is being evaluated is given by

$$\varphi = 2\pi(px + qy + rz).$$

If this value is substituted in a Fourier series for the electron density, $\rho(xyz)$, at (xyz), we obtain

$$\rho(xyz) = \sum_{p,q,r=-\infty}^{+\infty} K(pqr) \exp 2\pi i(px + qy + rz)$$

This equation can be substituted in the general expression for the structure factor to give

$$F(hk\ell) = V\int_0^1\int\int \left\{\sum_{p,q,r=-\infty}^{+\infty} K(pqr)\exp 2\pi i(px + qy + rz)\right\} \exp 2\pi i(hx + ky + \ell z)\, dx\, dy\, dz$$

$$= \sum_{p,q,r=-\infty}^{+\infty} V\int_0^1\int\int K(pqr)\exp 2\pi i\left[(p+h)x + (q+k)y + (r+\ell)z\right] dx\, dy\, dz$$

The integral has the value zero unless

$$h = -p, \quad k = -q, \quad \ell = -r,$$

when $F(hk\ell) = V\int_0^1\int\int K(\bar{h}\bar{k}\bar{\ell}) \exp 0\, dx\, dy\, dz = V\, K(\bar{h}\bar{k}\bar{\ell})$

$$\text{i.e.} \quad K(\bar{h}\,\bar{k}\,\bar{\ell}) = \frac{F(h\,k\,\ell)}{V}$$

The three-dimensional Fourier synthesis can now be written:

$$\rho(xyz) = \frac{1}{V} \sum_{h,k,\ell=-\infty}^{+\infty} \sum F(hk\ell) \exp - 2\pi i\,(hx + ky + \ell z).$$

A special case is the zero term in the summation when $h = k = \ell = 0$. Here

$$K(000) = \frac{F(000)}{V} = \frac{Z}{V} .$$

where Z is the number of electrons in the unit cell. This term is therefore independent of the way in which the atoms are distributed in the unit cell.

The Fourier coefficients are, in general, complex and may be written

$$F(hk\ell) = A(hk\ell) + i\,B(hk\ell).$$

As the electron density must be real, then

$$|F(hk\ell)| = |F(\bar{h}\bar{k}\bar{\ell})|,$$

$$\text{i.e.} \quad A(hk\ell) = A(\bar{h}\bar{k}\bar{\ell}),$$

$$B(hk\ell) = -B(\bar{h}\bar{k}\bar{\ell}).$$

The series can therefore be written as

$$\rho(xyz) = \frac{1}{V}\left\{F(000) + \sum_{-\infty}^{+\infty}\sum A(hk\ell) \cos 2\pi(hx + ky + \ell z) + B(hk\ell) \sin 2\pi(hx + ky + \ell z)\right\}$$

$$= \frac{1}{V}\left\{F(000) + \sum_{-\infty}^{+\infty}\sum |F(hk\ell)| \cos\left[2\pi(hx+ky+\ell z) - \alpha(hk\ell)\right]\right\}$$

1.7. The Intensity of an X-ray Reflexion.

In the previous sections, it has been shown that the structure factors for all planes can be calculated from a knowledge of atomic positions and, conversely, the electron density can be evaluated from the structure factors. Unfortunately, it is not possible to observe directly the structure factors; it is necessary to make use of a related quantity, "the integrated intensity". If the crystal is rotated through the reflecting position with angular velocity, w, and the total reflected energy recorded on the photographic film is $E(hk\ell)$, then the "integrated intensity" is the ratio $E(hk\ell)w/I_o$ where I_o is the intensity of the incident beam.

It can be shown that for a mosaic crystal the relationship between the integrated reflexion and the structure amplitude is given by

$$\frac{E(hk\ell)w}{I_o} = K_n L p \left|F(hk\ell)\right|^2 .$$

K_n is a constant for the experiment; $K_n = \left[\frac{\lambda^3 N^2 \, dV}{2\pi}\right] \frac{e^4}{m^2c^4}$,

where dV is a small volume of crystal.

L is the Lorentz factor and takes into account the motion of the crystal with respect to the incident beam.

p is the polarization factor which makes the necessary

allowance for the random polarisation of the incident beam. It is a simple function of the Bragg angle, θ, and is given by

$$p = \frac{1 + \cos^2 2\theta}{2} .$$

The integrated intensities can be measured from the blackening of the photographic film by comparison with a set of spots of similar shape whose relative intensities are known. As K_n is not normally known, comparison with arbitrarily scaled intensities is no disadvantage; this gives structure amplitudes on a relative scale.

1.8. The Phase Problem.

The electron density at any point in the crystal lattice can be evaluated by summing a Fourier series, in which the coefficients are the structure factors. The modulus of the structure factor can be obtained from the relationship between the integrated intensity and the square of the structure factor; the phase, on the other hand, cannot be determined experimentally. The determination of the unknown phases is the central problem of X-ray crystallography.

One method of overcoming this problem is to prepare by chemical methods compounds which contain one or more atoms which is of greater atomic number than the other

atoms (Robertson and Woodward, 1937; 1940). The position of this atom in the lattice may be determined from the Patterson function and be used to calculate a phase for each reflexion. As this atom is heavier than the remainder, it will make the major contribution to each structure factor and an approximation to the true electron density will be obtained by summing a Fourier series with the observed structure amplitudes and these calculated phases. From the electron-density distribution, atomic positions for some, if not all, of the remaining atoms are found. The process of phase determination is repeated with the new atomic positions until a set of reliable phases are determined. Examples of this method are to be found in recent work in this department on natural products. (Arnott et al., 1961.)

The possibility of phase determination also occurs if two isomorphous crystals are available in which there is one replaceable atom. An early example of this is the elucidation of the structure of phthalocyanine derivatives by studying the metal-free, nickel, copper and platinum compounds. (Robertson 1935; 1936.)

1.9. The Patterson Function.

One of the routes to the solution of the phase problem is the use of the summation first suggested by Patterson (1934; 1935). This series is similar to a Fourier series but uses the square of the structure amplitude instead of the complex structure factor.

The electron density in a crystal is given by:

$$\rho(x,y,z) = \frac{1}{V} \sum_{h,k,\ell=-\infty}^{+\infty} \sum \sum F(hk\ell) \exp - 2\pi i(hx + ky + \ell z).$$

A similar expression may be obtained for

$\rho(x+u,\ y+v,\ z+w)$,

$$\rho(x+u,y+v,z+w) = \frac{1}{V} \sum_{h',k',\ell'=-\infty}^{+\infty} \sum \sum F(h'k'\ell') \exp -$$

$$2\pi i\left[h'(x+u) + k'(y+v) + \ell'(z+w)\right].$$

The product of these two electron-density functions is formed and integrated over the unit cell to describe the Patterson function $P(u,v,w)$ where

$$P(u,v,w) = \int_0^1 \rho(xyz).\rho(x+u,\ y+v,\ z+w)\ dv.$$

$$= V \int_0^1\int\int \rho(xyz)\ \rho(x+u,\ y+v,\ z+w)\ dx\ dy\ dz.$$

The two functions may be expanded in terms of their Fourier series.

The integrals of each of the products formed by term-by-term multiplication are zero except when

$$h = -h' \quad , \quad k = -k' \quad , \quad \ell = -\ell' .$$

This series therefore becomes

$$P(uvw) = \frac{1}{V} \int_0^1\int_0^1\int_0^1 \sum_{h,k,\ell=-\infty}^{+\infty} F(hk\ell)\ F(\bar{h}\bar{k}\bar{\ell}) \exp 2\pi i\ (hu + kv + \ell w)\ dx\ dy\ dz$$

$$= \frac{1}{V} \sum_{h,k,\ell=-\infty}^{+\infty} F(hk\ell).\ F(\bar{h}\bar{k}\bar{\ell}) \exp 2\pi i(hu + kv + \ell w).$$

The terms $F(hk\ell)$ and $F(\bar{h}\bar{k}\bar{\ell})$ are complex conjugates and their product is equal to $|F(hk\ell)|^2$. As this expression is found from the intensity directly, there is no uncertainty in phase.

If the distribution of P(uvw), which has the same unit cell dimensions as the true unit cell, ,is plotted, peaks occur at the point (uvw) when the vector, $\underline{r} = u\underline{a} + v\underline{b} + w\underline{c}$, represents a vector joining two atoms, i.e. when $\rho(xyz)$ and $\rho(x+u,\ y+v,\ z+w)$ are both large. A large peak occurs at the origin caused by the products of all the atoms with themselves. The height of the peak depends on the electron-density heights of the atoms causing it. Thus, a heavy atom in the structure will give rise to relatively high Patterson peaks and

the effect is used to give the positions of the heavy atoms and, in some cases, of the light atoms in the real unit cell.

1.10. Refinement of a Structure.

After an initial structure has been obtained, it is necessary to adjust the atomic parameters for each atom to give the best agreement between the observed structure amplitudes and the calculated structure factors. The process of improvement is known as "refinement" of a structure.

Successive Fourier syntheses are used in refinement. This consists of computing the electron density by normal methods, obtaining the parameters of each atom from the electron-density values at a grid of points in the neighbourhood of the atoms, then using these coordinates to calculate new phases and repeating the complete process. Although an infinite number of terms ought to be summed in the Fourier series, there is an experimental limitation in the number of terms available. The result of having only a finite number of terms is that the peaks, although they are perfectly resolved, are surrounded by ripples which cause the observed peak to be displaced from its true position. This error is known as the termination-

of-series error. It can be overcome by applying to the observed coordinates a correction which may be estimated by summing the Fourier series with structure factors calculated from these coordinates, for the same number of terms and calculating new coordinates.

The second method of refinement used extensively in this thesis is that based on the least-squares technique from the theory of errors. This method was first suggested by Hughes (1941) and used by him in a two-dimensional refinement of the structure of melamine.

If the parameters defining the almost-correct structure are $u_1, u_2, \ldots, u_n$, then the structure factor is some function of these parameters

$$F_c = f(u_1, u_2, \ldots, u_n).$$

A similar expression holds for the observed structure amplitude,

$$F_o = f(u_1 + \epsilon_1, u_2 + \epsilon_2, \ldots, u_n + \epsilon_n)$$

where $\epsilon_1, \epsilon_2, \ldots, \epsilon_n$ are the shifts required to give the true structural parameters.

If the starting structure is a good approximation then $\epsilon_1, \epsilon_2, \ldots \epsilon_n$ will all be small and the equation for F_o can be expanded by Taylor's series,

$$F_o = f(u_1, u_2, \ldots, u_n) + \sum_{i=1}^{n} \frac{\partial f(u_1, u_2, \ldots, u_n)}{\partial u_i} \epsilon_i ,$$

where the second and higher order differentials are neglected.

$$\text{i.e.} \quad F_o = F_c + \sum_{i=1}^{n} \frac{\partial F_c}{\partial u_i} \epsilon_i ,$$

$$\text{i.e.} \quad (F_o - F_c) = \sum_{i=1}^{n} \frac{\partial F_c}{\partial u_i} \epsilon_i .$$

An equation of this type may be derived for all the reflexions. Each F_o is subject to random errors of observation and suitable values of ϵ_i have to be found to give the most acceptable fit between the observed structure amplitudes and the calculated structure factors. The theory of errors predicts that the most acceptable set of ϵ_i is that which minimises the sum of squares of the error, $(|F_o| - |F_c|)$,

$$\text{i.e.} \sum_{h,k,\ell} \sum \sum (|F_o| - |F_c|)^2 = \sum_{h,k,\ell} \Delta^2 .$$

A weighting factor can be introduced, $\sqrt{w}$, which depends on the reliability of the observed structure amplitude. The criterion that $\sum w \Delta^2$ should be a minimum leads to a set of simultaneous equations, the normal equations,

$$\sum_{h,k,\ell} w \Delta \frac{\partial F_c}{\partial u_i} = \sum_{h,k,\ell} w \left(\frac{\partial F_c}{\partial u_i}\right)^2 \epsilon_i + \sum_{h,k,\ell} w \frac{\partial F_c}{\partial u_i} \left\{ \sum_{j \neq i}^{n} \frac{\partial F_c}{\partial u_j} \cdot \epsilon_j \right\},$$

or $$b_j = \sum_{i=1}^{n} \epsilon_i a_{ij}, \quad \text{(Matrix Notation.)}$$

Certain assumptions are now made which simplify the arithmetic involved. If the parameters are all coordinates referred to orthogonal axes and there is sufficient data available to avoid overlap, then the off-diagonal terms of the matrix, i.e. the second term of the first equation or $a_{ij}(i \neq j)$ in the second equation are negligible and the solution of the equations becomes

$$\epsilon_i = \sum_{h,k,\ell} w \Delta \frac{\partial F_c}{\partial u_i} \Big/ \sum_{h,k,\ell} w \left(\frac{\partial F_c}{\partial u_i}\right)^2 .$$

The least-squares program used in the refinements to be described refines three positional parameters, six thermal parameters per atom and an overall scale factor. The program solves the normal equations using 3 x 3 and 6 x 6 block-diagonal matrices for the positional and thermal parameters, respectively, of each atom in turn and a 2 x 2 matrix for the scale factor. This takes into account interaction between the positional parameters,

in one case, and the thermal parameters, in the second case, of any one atom but not general interatomic interaction. (Rollett, 1961.)

1.11. Estimate of Accuracy.

The normal equations are of the form

$$\sum_{i=1}^{n} \epsilon_i a_{ij} = b_j .$$

The variance of the parameter u_j is given by

$$\sigma^2(u_j) = a^{jj} .$$

where a^{jj} is an element of the matrix, A^{-1}, which is the inverse of the matrix, A, whose elements are given by a_{ij}.

This result is applicable when the absolute weights are known. In the case where the relative weights are known, the estimated standard deviations, $s(u_j)$, is given by

$$s^2(u_j) = a^{jj} \sum w \Delta^2/(m-n),$$

where (m-n) is the excess of the number of reflexions (m) over the number of parameters (n).

If off-diagonal terms are negligible then

$$a^{jj} = 1/a_{jj} = 1/\sum_{h,k,\ell} w\left(\frac{\partial F_c}{\partial u_j}\right)^2$$

i.e. $s^2(u_j) = \sum w \Delta^2/(m-n) \sum w \left(\frac{\partial F_c}{\partial u_j}\right)^2$.

In this way the standard deviation of the parameters can be determined from the least-squares residuals.

Dunitz and Rollett (1956) suggest that, for monoclinic space groups, to offset the effects of neglecting off-diagonal terms in the derivation of this expression, $\sigma(x)$ and $\sigma(z)$ be multiplied by the angle, β , in right angles.

From the standard deviations of two atoms, the standard deviation of the bond length joining them, $\sigma(d_{12})$, can be calculated. This quantity is important in deciding whether the difference, $\delta\ell$, between measurements, which are subject to error, obtained for supposedly identical bonds is meaningful. Cruickshank has suggested the following levels of significance :-

$\delta\ell \leqslant 1.645\ \sigma(d_{12})$, the difference is not significant.

$2.327\ \sigma(d_{12}) > \delta\ell > 1.645\ \sigma(d_{12})$, the difference is possibly significant.

$3.090\ \sigma(d_{12}) > \delta\ell > 2.327\ \sigma(d_{12})$, the difference is significant.

It has become customary to follow the course of an analysis in terms of the "reliability index", R, which is defined by

$$R = \sum_{h,k,\ell} |F_o - F_c| \Big/ \sum_{h,k,\ell} |F_o| \ .$$

CHAPTER 2.

THE CRYSTAL STRUCTURES OF, AND HYDROGEN BONDING IN THE ACID SALTS OF SOME MONOBASIC ACIDS.

Section 1. INTRODUCTION.

2.1.1. Hydrogen Bonding.

In 1920, Latimer and Rodebush, in an explanation of the properties of associated liquids, proposed that "the hydrogen nucleus held between two octets constituted a weak bond". From this starting point, the importance of hydrogen bonding in every type of molecular association, including crystals, was quickly realised. The hydrogen bond, A - H ..... B, is usually considered to be a bond in which a hydrogen atom lies between two closely spaced electronegative atoms, A and B. The atoms A and B are normally oxygen, nitrogen, fluorine, chlorine and bromine. A hydrogen-bonded system is most easily identified by its properties of which the two most important are the distance between A and B and the changes occurring in the vibrational spectra of A - H.

X-ray diffraction methods are used to provide the A....B distances in crystals; the results obtained have been reviewed by Donohue (1952). The distances observed are always less than the sum of the normal van der Waals distances. Donohue stresses that, almost without exception, molecules in crystals arrange themselves so

that the maximum number of hydrogen bonds is formed. This view is supported by Fuller (1959) in a more recent review of hydrogen bond lengths and angles in crystals. Fuller constructs histograms for the lengths of various types of hydrogen bonds and the angles at the hydrogen donor atom between the hydrogen bond and the expected direction of the bond between the donor atom and the hydrogen. In particular, he gives the distance O .... O for hydrogen bonds in dimeric carboxylic acids as 2.65 ± 0.05Å. Although the X-ray method provides the distance between the two atoms participating in the hydrogen bond, the position of the hydrogen atom itself is not normally identified. Neutron-diffraction techniques, however, can be used to provide direct evidence of the hydrogen atom and several compounds containing hydrogen bonds have been studied (e.g. Bacon and Curry, 1956; 1960).

The other most informative property of the hydrogen bond is the effect which hydrogen bonding has on the vibrational spectra of A - H. These spectra have been studied extensively and attempts have been made to correlate the spectroscopic data, the length and the strength of the hydrogen bond. Rundle and Parasol (1952) noticed that there was a tendency in short O - H .... O

distances for the O - H stretching frequency to become broad, indistinct and displaced so as to become unrecognizable. This was supported by Lord and Merrifield (1953) in their paper on strong hydrogen bonds in crystals. Nakamoto, Margoshes and Rundle (1955) considered further this relationship between the stretching frequency and the length of the hydrogen bond and produced a figure of the O - H distance plotted against the O - H .... O distance. From this figure, they suggested that for hydrogen bonds between oxygen atoms of length $\sim$ 2.45 Å, the hydrogen atom will be centred.

Meanwhile, in this laboratory, the structures of the acid salts of monobasic carboxylic acids were under study and it had been shown that these salts contain short and, in some cases, crystallographically-symmetrical hydrogen bonds (e.g. Speakman, 1949).

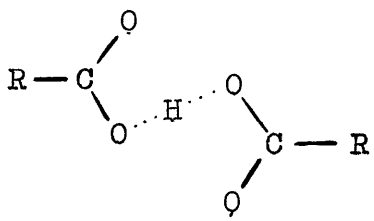
2.1.2. Acid Salts of Monobasic Carboxylic Acids.

Many monobasic carboxylic acids readily form crystalline acid salts with a variety of metals. These salts are formed by the combination of one molecule of the neutral salt and one or more molecules of the parent acid. In this case, some 1:1 acid salts have been prepared and

studied, i.e. one molecule of the free acid (R.COOH) has combined with one molecule of the neutral salt (R.COOM) to give the acid salt, $MH(R.COO)_2$.

Although the existence of these acid salts has been known for over a century, the nature of the linkage between the acid and the salt has been the subject of speculation. Thermochemical measurements by de Forcrand (1883) and Rivals (1897) established that some linkage did exist and later authors (e.g. Farmer, 1903; Pfeiffer, 1914; Ross and Morrison, 1933) have proposed various structural formulae. The first direct evidence of the crystal structures of the acid salts was provided when Speakman (1949) applied X-ray crystallographic methods.

The results of the work in this laboratory show that the acid salts fall into two structural types, A and B. In type A, the acidic residue of the salt ($R.COO^-$) and the acid (R.COOH) are related by an element of symmetry and hence it is impossible to distinguish between them, e.g.



The oxygen atoms of the two related residues are

linked by a very short hydrogen bond, in all cases, shorter than the 2.65 Å quoted by Fuller for dimeric carboxylic acids.

In type B, on the other hand, the acidic residues are crystallographically distinct and the anion ($R.COO^-$) and the neutral molecule of the acid (R.COOH) can be identified. A short hydrogen bond is formed between the two residues but, in this case, it is no longer joining symmetry-related atoms.

Examples of types A and B are given in the final discussion.

2.1.3. Infrared Spectra of Acid Salts.

After the type A acid salts had been shown to contain short and, apparently, symmetrical hydrogen bonds, the infrared spectra of a number of these compounds were studied by spectroscopic methods (Hadzi and Novak, 1955; 1960; Albert and Badger; 1958). They noticed that the two types gave different types of infrared spectra.

The spectra of type A were not compatible with a simple superposition of the spectra of the neutral salt and the free acid. The most important features were

the absence of a bond above 1700 $cm.^{-1}$ which could be attributed to the O - H stretching frequency and the broad bond of absorption below 1600 $cm.^{-1}$. They concluded from this that the hydrogen bond must be of the single-minimum symmetrical type (Sheppard, 1959). In type B acid salts, they identified strong bonds of absorption in the infrared spectrum attributable to the O - H stretching vibration and, overall, the spectrum approximates to a superposition of the spectra of the free acid and the neutral salt. Hadzi used infrared spectroscopy to classify the potassium acid salts of o-nitrobenzoic and p-nitrobenzoic acids into type A and type B respectively. This classification has been confirmed by X-ray analysis (Shrivastava and Speakman, 1961).

Section 2. THE CRYSTAL STRUCTURE OF SODIUM HYDROGEN DIACETATE.

2.2.1. Introduction.

Acid salts of acetic acid have been known since the beginning of the nineteenth century when they were first prepared by Thomson. Villiers, in 1877, describes a series of sodium acid salts of acetic acid. He includes one forming cubic crystals and to this he assigns a formula which includes water of crystallisation. Lescoeur (1877), at the same time, was studying these acid salts and describes the same crystals but gives a formula which has no water of crystallisation. Villiers, in a later paper, corrects his formula to agree with that of Lescoeur. The formula is essentially one molecule of sodium acetate added to one molecule of acetic acid, in other words sodium hydrogen diacetate, $NaH(CH_3.COO)_2$.

The morphology was studied by Haushofer (1880) who showed that the crystals belonged to the cubic system. The classification to a particular symmetry class on classical crystallographic evidence was never made. Wyckoff (1922), during an investigation of cubic crystals by X-ray methods, used this substance as an example and studied it extensively; he deduced the correct space

group, Ia3 (T_h^7), from Laue photographs and describes the structure as being 24 molecules of sodium hydrogen diacetate in a cubic unit cell of dimension 15.98 Å.

2.2.2. Summary of Previous Work.

The structure of sodium hydrogen diacetate had been determined by Dr. J.C. Speakman (1959). The space group, Ia3, is centrosymmetric and the positions of only five atoms are needed to define the structure. This task proved impossible when only two-dimensional methods were available since the high symmetry causes extensive overlap. The diagram illustrating the projection of part of the structure shows this clearly. When the computor DEUCE became available for the rapid calculation of three-dimensional electron-density syntheses, the structure was solved by trial-and-error methods after a careful consideration of possible packing and bonding arrangements in the crystal. Refinement proceeded by the Fourier and least-squares methods on 195 terms.

The object of the work to be described was to extend the data and use them in further refinement.

2.2.3. Crystal Data.

The crystal and physical data obtained for sodium hydrogen diacetate are as follows :-

$NaH(C_2H_3O_2)_2$ M = 142.09

Cubic, $a = 15.92 \pm 0.01$ Å.

Volume of unit cell = 4035 $Å^3$.

ρ obs. = 1.40; calculated on basis of 24 molecules in the unit cell, ρ = 1.403.

F(000) = 1776

Linear absorption coefficient for X-rays, $\mu = 17.6 cm.^{-1}$

Absent spectra : (hk0) h = 2n+1, k = 2n+1
(correspondingly for h0ℓ and 0kℓ)
(hkℓ) h + k + ℓ = 2n + 1.

Space Group : $Ia3 - T_h^7$.

2.2.4. Intensity Data.

Intensity data for the hk0, ..., hk8 reciprocal lattice nets and for the diagonal projection were estimated visually from Weissenberg photographs by comparison with a calibrated intensity scale using the multiple-film technique (Robertson, 1943). The film factor used to correlate the intensities on successive photographs of a series in upper-layer lines was modified by the function,

$$R = 1.29 \exp (0.942 \sec v),$$

where v is the angle which the incident beam makes with the normal to the film (Rossmann, 1956). Cu Kα radiation was used throughout.

The intensities were corrected by means of the Lorentz and polarization factors given by the formula,

$$I(hk\ell) = \frac{1}{\sin 2\theta} \frac{1 + \cos^2 2\theta}{2} |F(hk\ell)|^2 .$$

This form of the Lorentz factor is only applicable when the reflexion is from a plane parallel to the rotating axis and the X-ray beam is directed perpendicular to this axis. These conditions do not apply to upper-layer data and an additional rotation factor must be applied to the intensities.

For normal-beam Weissenberg photographs, this correction, R, is given by

$$R = (\sin^2\alpha - \sin^2\theta)^{\frac{1}{2}} / \cos\theta ,$$

where θ is the Bragg angle and α is the angle between the axis of rotation and the normal to the crystal plane (Cox and Shaw, 1930). This correction was applied to the hk1, ..., hk5 data which were collected by the normal-beam technique.

For equi-inclination Weissenberg photographs, where the rotation axis of the crystal is inclined to

the X-ray beam at an angle, u, equal to that made by the rotation axis and the reflected beam for the layer-line being analysed, the rotation factor required is given by : (Tunell, 1939)

$$D = (\cos^2 u - \cos^2\Theta)^{\frac{1}{2}} / \sin\Theta .$$

No absorption corrections were applied.

The application of these corrections gave structure amplitudes for each zone on a relative scale. Since, in this space group,

$$F(hk\ell) = F(k\ell h) = F(\ell hk),$$

many reflexions were observed on three independent occasions. This relationship and the data from the diagonal net enabled the zones to be scaled relative to each other.

The variance of the observations of some 85 reflexions which were measured three times was assessed from the equation,

$$\sigma^2 F(hk\ell) = \sum_{r=1}^{3} |\langle F\rangle - F_r|^2/(n-1),$$

where n has the value three.

The results indicated that $\sigma F(hk\ell) = 0.094\,|F(hk\ell)|$.

The observed structure amplitudes were established on an absolute scale by equating the sum of the structure factors calculated on the basis of the final structure

obtained by Speakman for the 195 reflexions measured by him to the sum of the observed structure amplitudes for the same reflexions using the new values obtained.

The structure amplitudes of 525 reflexions were now available for further refinement. As the total number of reflexions observable with Cu Kα radiation is 755, this represents 43% coverage. If the region of reciprocal space is curtailed at $2 \sin\theta = 1.58$, which corresponds to half the sphere of reflexion, the coverage is 65%.

2.2.5. First Phase of Refinement.

Refinement proceeded by the least-squares method and a summary of the course of refinement is shown in Table 1.

The function minimised is

$$\sum_{h,k,\ell} w(hk\ell)\left[K|F_o| - |F_c|\right]^2 = \sum_{h,k,\ell} w\Delta^2,$$

where F_o is the observed structure amplitude, $w(hk\ell)$ is the weighting factor for the $(hk\ell)$ reflexion and K is the overall scale factor.

Three weighting systems are available in Rollett's program (Rollett, 1961). The first two are simple

TABLE 1.

Sodium Hydrogen Diacetate:

Progress of Refinement.

Cycle	R^*	Notes
1	14.1	
2	11.5	KF* increased to 14.08; Hydrogen contribution included in S.F.
3	10.7	
4	9.7	
5	9.3	Includes unobserved terms in solve.
Final Structure Factors	9.2	

* Observed terms only.

functions of $|F_o|$ and are as follows ;

$\sqrt{w_1}$; $\sqrt{w_1} = 1$ if $|F_o| < F^*$, $\sqrt{w_1} = F^*/|F_o|$ otherwise.

$\sqrt{w_2}$; $\sqrt{w_2} = |F_o|/F^*$ if $|F_o| < F^*$, $\sqrt{w_2} = F^*/|F_o|$ if $F^* < |F_o|$.

In these two schemes F^* is a constant. The third scheme allows the weight for each $|F_o|$ to be assigned individually and be included in the input data.

The $\sqrt{w_2}$ scheme was used in this refinement with F^* set equal to 12.80 in the first cycle and raised to 14.08 in subsequent cycles. The latter value is approximately equal to $\langle F_c \rangle$.

For the structure-factor calculations the following theoretical atomic scattering factors were used; for carbon the curve calculated by Berghuis et al.(1955), for the sodium ion Freeman's function was used and for the oxygen atom a scattering curve was derived in the following way from Freeman's values. The oxygen atoms may be regarded as ionic with a proton between a pair of oxygen atoms. For this reason, a scattering curve corresponding to $O^{-\frac{1}{2}}$ was obtained by averaging, at each value of $\sin\Theta$, the values of O and O^- given by Freeman (1959). For the sodium ions in special positions, the scattering-factor curve is scaled down by a factor

appropriate to the multiplicity of the special position in which the atom occurs; Na(2) requires one-third scale factors whereas Na(1) uses one-sixth scale factors.

The position of Na(1) is fixed by the space group and was not included in the refinement. Na(2), which is sited on a three-fold axis with coordinates (x,x,x), was included. The results of the Gauss-Seidel iteration used in the solution of the three identical normal equations produced for the shifts ϵ_x, ϵ_y and ϵ_z gave $\epsilon_y = \epsilon_z = 0$ and ϵ'_x with three times its true value. This was easily adjusted to give $\epsilon_x = \epsilon_y = \epsilon_z$ and produce new coordinates for Na(2), $(x + \epsilon_x, x + \epsilon_x, x + \epsilon_x)$. The temperature factors were treated in a similar way.

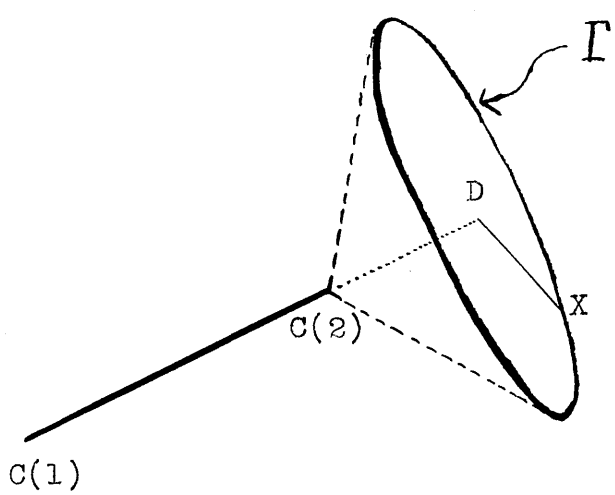
Half-shift corrections were used throughout the refinement.

The final coordinates and temperature parameters obtained by Speakman in the refinement using 195 reflexions were used as the starting point of this refinement.

The space group is centrosymmetrical and hence the structure-factor calculation need use only one-half of the equivalent positions; in addition, the indexing of reflexions accounts for the body centring. This means that only 12 out of the 48 equivalent positions are required in the calculation and the structure factors obtained are on one-quarter scale.

2.2.6. Coordinates of the Hydrogen Atoms.

After two cycles of least-squares refinement, it was decided to assess if it would be worthwhile including the hydrogen atoms of the methyl group in the structure-factor calculation. Two criteria would have to be satisfied before this step could be considered justified; evidence of hydrogen atoms would have to be obtained from Fourier difference maps and structure factors calculated including the hydrogen atom positions would require to show better agreement with the observed data than those calculated formerly. From the known positions of C(1) and C(2) and the assumption of a carbon-hydrogen bond length of 1.1 Å (Dewar and Schmeising, 1959), it is possible to calculate the locus of the hydrogen atoms of the methyl group in space, Γ.



C(1) - C(2) 1.47 Å
C(2) - H 1.1 Å

Fig. V.

Γ is defined as the intersection of the sphere, with centre D and radius DX (DX = 1.057 Å), and the plane through D perpendicular to the bond joining C(1) and C(2).

The cell edges describe the orthogonal axes required for the analytical geometry. Fractional coordinates are used.

The equation of the plane is

$$881\ (x - 0.200) + 195\ (y - 0.363) = 209(z - 0.084)$$

and of the sphere is

$$(x - 0.200)^2 + (y - 0.363)^2 + (z - 0.084)^2 = (0.0651)^2.$$

Three difference Fourier maps were calculated for sections parallel to the (100) plane and cutting Γ (which is in fact a circle) to give the maximum information. These are given in Fig.VI where the sections are perpendicular to the x-axis and hence are inclined at a small angle to the C(1) - C(2) bond.

The three hydrogens are regularly placed round the circle, Γ, and if the coordinates of one are fixed, then those of the other two may be calculated. The coordinates of one of the hydrogens were taken from the well-resolved peaks in the difference map and adjusted to lie on the circle; those of the remaining two were now calculated. The coordinates calculated are shown by crosses in Fig.VI, and are included in Table 4.

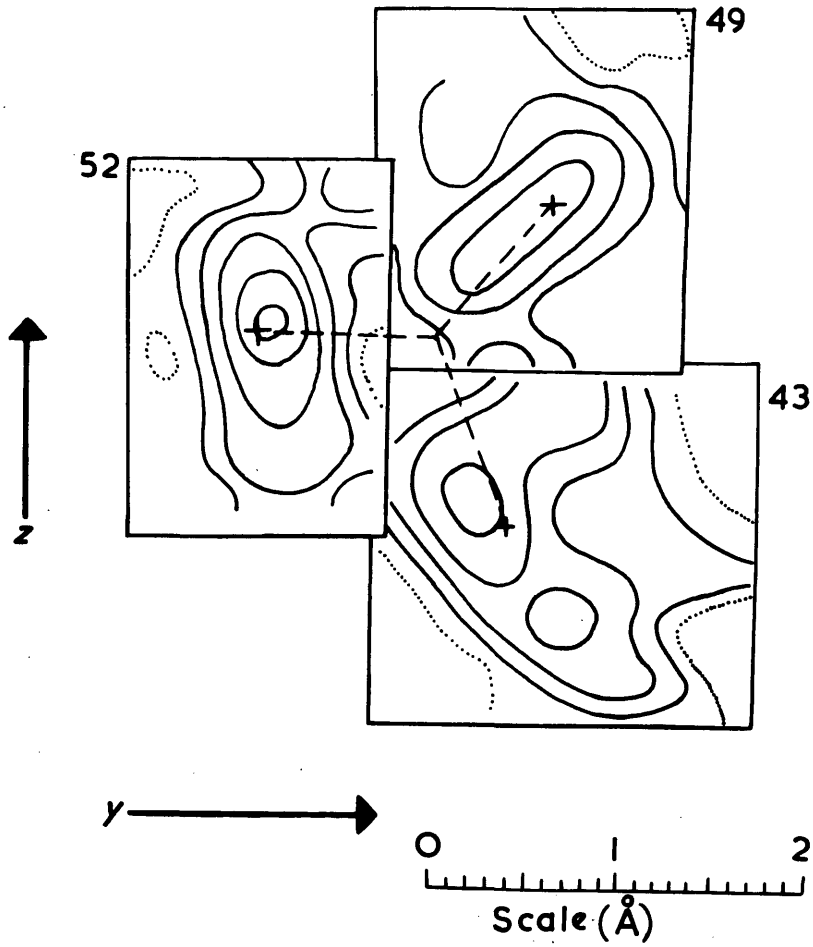


Fig.VI. Sodium Hydrogen Diacetate: Electron-density difference synthesis for sections at x = 49/240, 43/240 and 52/240, covering the region of the methyl-hydrogen atoms. C-H bonds are indicated by broken lines. Contour-line interval : 0.1 electron per cubic Å, with the zero line dotted.

When the hydrogen coordinates were included in structure-factor calculations, with B = 4 $\mathring{A}^2$, it was found that agreement for the low-order terms showed marked improvement while there was a slight worsening of the high-order terms. When the temperature factor was increased to 7, the improvement was retained but the second effect was eliminated.

The hydrogen of the hydrogen bond was included in the structure-factor calculation with coordinates on the two-fold axis $(0,\frac{1}{4},z)$ and the z-coordinate of O(2). In this case, a temperature factor of B = 4 $\mathring{A}^2$ was retained. The McWeeny (1951) scattering curve for hydrogen was used.

2.2.7. Final Phase of Refinement.

The refinement continued for a further two cycles with the inclusion of the hydrogen atoms in the structure-factor calculation. At the conclusion of each cycle of refinement, bond lengths were calculated.

The structure factors for all the reflexions which were not observed on the films were calculated in the range, $0 < \sin^3\theta < 0.5$. From some 135 missing reflexions in this range, 29 had F_c values which implied that the

reflexions should have been observable. These reflexions were now included in the least-squares refinement with an observed structure amplitude equal to half the minimum locally observable. One final cycle of least-squares refinement completed this analysis.

The refinement of the thermal parameters of Na(1) was not attempted but prior to the calculation of the final structure factors the thermal parameter was adjusted to be smaller than that of Na(2) in proportion to the electron-density peak heights observed in the final Fourier sections. Na(1) appeared to a height of 23.9 electrons $\mathring{A}^{-3}$ against 21.7 electrons $\mathring{A}^{-3}$ for Na(2).

The final structure factors and observed structure amplitudes are shown in Table 2; the unobserved reflexions used in the refinement are also included but the $|F_o|$ value quoted is the local minimum observable. The values in this table are on full-scale.

The final value of R is 9.2% and this is increased to 10.9% if the unobserved terms are included. Structure factors based on the final atomic coordinates but excluding the hydrogen atoms gave values of R of 9.7% and 11.4% respectively.

It will be noticed that for the reflexion (004), the F_c value greatly exceeds the $|F_o|$ value. This

difference was apparent at an early stage of the refinement and was attributed to extinction. Accordingly, a value of $|F_o|$ almost equal to F_c was included in the least-squares cycles for this reflexion; the higher value was used in calculating R.

The final anisotropic temperature-factor parameters are shown in Table 3; they are values of b_{ij} in the equation,

$$\exp(-B \sin^2\Theta/\lambda^2) = 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + b_{12}hk + b_{23}k\ell + b_{31}\ell h)}.$$

This table also includes the thermal parameters parallel to each principal axis. This conversion makes use of the relationships,

$$\beta_{11} = a^{*2}B_x/4 \quad \text{and} \quad b_{11} = 1.4427\,\beta_{11}.$$

(Cruickshank, 1956; Rossmann, Jacobson, Hirshfeld, and Lipscomb, 1960; Rollett, 1961.)

2.2.8. Molecular Dimensions.

Table 4 lists the final atomic coordinates given by the least-squares refinement.

The penultimate structure factor phases were used in the calculation of electron-density sections through

TABLE 8.

Sodium Hydrogen Diacetate:
Observed structure amplitudes
and calculated structure factors.

h	k	ℓ	$\|F_o\|$	F_c	h	k	ℓ	$\|F_o\|$	F_c
0	0	2	144	+158	0	4	12	26	+ 13
		4	291	-508			14	70	+ 79
		6	163	-167			16	29	+ 33
		8	223	+253			18	18	+ 22
		10	115	+121	0	6	2	162	+166
		12	30	+ 36			6	34	- 24
		14	59	- 59			8	28	+ 20
		18	24	+ 28			10	105	+ 97
0	2	2	39	+ 28			14	63	+ 65
		4	166	+192			16	46	+ 48
		6	20	- 7			18	21	+ 22
		8	57	+ 57	0	8	2	173	+193
		10	94	+ 90			4	137	-133
		12	53	+ 57			6	43	- 34
		14	52	- 45			8	70	+ 66
		18	39	+ 43			10	101	+111
0	4	2	96	- 96			16	20	+ 22
		4	199	+206			18	13	- 4
		6	220	+238	0	10	2	52	+ 50
		8	58	+ 50			4	55	+ 53
		10	47	- 43			6	74	+ 84

- Cont'd -

TABLE 2. (Cont'd)

h	k	ℓ	$\|F_o\|$	F_c
0	10	8	33	+ 32
		10	30	+ 29
		12	21	+ 19
		14	20	- 19
0	12	2	39	- 39
		4	108	+108
		6	109	+108
		10	52	- 49
		12	48	+ 46
		14	20	+ 18
0	14	2	27	- 17
		4	127	+130
		6	24	+ 16
		8	26	- 22
		12	52	+ 56
		14	33	+ 40
0	16	2	29	+ 12
		8	45	+ 41
0	18	2	30	+ 43
		10	29	+ 36
0	20	2	24	+ 35
1	1	2	110	-121
		4	70	- 72
		6	168	+200
		8	76	+ 72
		10	52	- 51
		12	30	-29
		14	37	+ 45
1	2	3	82	- 90
		5	15	+ 18
		7	43	+ 43
		9	38	+ 34
		11	30	- 29
		13	39	+ 45
		15	35	- 37
		19	30	+ 36
1	3	2	100	+104
		4	113	-106
		6	117	+118
		8	115	+113
		12	44	- 42
		14	57	+ 57

- Cont'd -

TABLE 2. (Cont'd)

h	k	ℓ	$\|F_o\|$	F_c
1	4	3	26	+ 21
		7	59	- 54
		9	28	+ 20
		13	44	+ 47
1	5	2	109	+116
		4	57	+ 60
		6	43	- 44
		8	114	-111
		10	35	+ 39
		12	69	+ 67
		16	57	- 64
1	6	3	64	- 68
		5	108	-108
1	6	9	54	+ 58
		13	19	- 22
		19	12	- 23
1	7	2	172	+186
		4	20	+ 17
		6	203	-202
		8	65	- 64
		10	65	+ 66
		14	40	- 41
1	8	5	56	- 50
		7	21	+ 11
		9	45	+ 46
		11	30	+ 37
		13	66	- 71
1	9	2	109	-105
		4	49	+ 51
		8	42	- 50
		10	31	- 22
		12	31	+ 28
1	10	3	33	+ 34
		5	34	+ 30
		9	32	- 37
		11	32	+ 30
1	13	2	36	+ 45
		8	29	+ 29
1	14	3	44	- 49
		5	43	- 52
		7	19	+ 22
1	15	2	43	+ 42
1	19	2	25	- 39

- Cont'd -

TABLE 3. (Cont'd)

h	k	ℓ	$\|F_o\|$	F_c
2	2	2	136	+148
		4	94	+ 92
2	2	8	24	+ 21
		10	73	+ 81
		12	41	+ 45
		18	29	+ 24
2	3	3	130	-138
		5	118	-116
		7	64	+ 63
		9	78	+ 75
		11	23	- 16
		13	63	- 65
2	4	4	24	+ 32
		6	21	+ 21
		10	29	+ 23
		12	69	+ 70
		14	69	+ 72
		16	29	+ 30
2	5	3	131	-126
		5	87	- 96
		7	101	- 96
		9	81	+ 79
2	5	11	50	- 21
		13	59	- 59
2	6	4	91	+ 99
		6	75	+ 74
		8	71	+ 64
		10	44	+ 42
		12	29	+ 17
		16	32	+ 27
		18	23	+ 24
2	7	3	59	- 64
		5	98	+ 99
		7	49	- 41
		9	38	- 36
		11	56	- 58
		13	33	+ 29
		15	32	+ 34
2	8	4	48	+ 47
		6	77	+ 69
		8	85	+ 76
		10	29	+ 28
		18	27	+ 24

- Cont'd -

TABLE 2. (Cont'd)

h	k	ℓ	$\|F_o\|$	F_c
2	9	5	71	+ 66
		7	48	+ 48
		11	36	- 35
		13	31	+ 28
		15	47	+ 46
2	10	4	36	+ 35
		10	36	+ 36
		12	30	+ 41
2	11	3	36	+ 36
		5	33	+ 30
		9	29	- 22
		11	65	+ 76
2	12	6	44	+ 35
		8	19	+ 27
		14	24	+ 29
2	13	3	100	+ 99
		5	97	- 99
		7	38	- 47
		11	33	+ 59
2	14	4	59	+ 62
		6	38	+ 51
3	3	6	107	-105
		8	50	+ 47
		10	39	+ 37
		14	77	- 80
3	4	7	51	- 51
3	4	9	37	+ 34
3	5	4	38	+ 32
		6	47	+ 40
		8	30	+ 21
		10	55	- 49
		16	36	+ 35
3	6	5	49	- 47
		7	105	+109
		9	85	+ 87
		11	68	- 63
		13	74	- 78
3	7	4	32	+ 23
		6	61	+ 55
		10	52	- 52
		14	59	+ 55
3	8	5	77	- 71
		7	19	- 21

- Cont'd -

TABLE 2. (Cont'd)

h	k	ℓ	$\|F_o\|$	F_c	h	k	ℓ	$\|F_o\|$	F_c
3	8	9	49	+ 42	4	5	9	32	- 29
		13	70	- 66			11	30	- 27
3	9	4	36	- 29	4	6	6	84	+ 76
3	10	7	36	- 34			10	32	- 26
		9	38	- 30			12	64	+ 62
		11	43	+ 42	4	7	5	21	- 26
3	11	4	55	- 58			7	42	+ 39
		8	40	+ 28	4	8	12	102	+ 95
		10	45	+ 45			14	45	+ 41
		12	39	- 38	4	9	5	32	- 30
3	14	5	60	- 55			7	26	+ 18
		7	51	+ 50			9	40	+ 34
		9	52	+ 41	4	10	8	72	+ 64
							10	67	+ 59
4	4	4	59	+ 51	4	11	5	69	+ 67
		6	135	+133			7	37	- 33
4	4	8	127	+120			9	38	- 35
		10	30	+ 24			11	33	+ 24
		12	41	- 29	4	12	8	70	+ 66
		14	22	- 30			10	66	+ 63
		16	22	+ 29			12	32	- 31
4	5	5	48	- 47	4	13	5	40	- 29

TABLE 2. (Cont'd)

h	k	ℓ	$\|F_o\|$	F_c
4	13	7	44	- 40
4	14	6	35	+ 28
		8	31	+ 26
		10	29	+ 33
4	16	6	27	+ 33
5	5	6	52	+ 50
		8	73	+ 67
		10	34	- 31
		12	43	- 45
		16	38	+ 46
5	6	9	85	- 79
		13	42	+ 46
		15	32	+ 30
5	7	6	146	+140
		8	60	+ 48
		10	44	- 40
		14	39	+ 43
5	8	7	21	+ 21
		11	46	- 50
5	9	8	68	+ 61
5	10	9	49	+ 57
		11	40	- 33
5	11	12	21	- 27
5	12	7	45	- 53
		9	39	+ 30
		11	34	+ 29
6	6	6	133	+122
		8	28	+ 26
		14	49	+ 42
6	7	9	32	- 32
		11	36	+ 38
6	8	8	21	+ 22
		10	48	+ 61
		12	43	+ 38
6	9	7	84	- 81
6	10	8	34	+ 36
		10	60	+ 64
6	10	12	32	+ 29
6	11	11	44	- 32
6	12	10	38	+ 29
6	13	7	52	+ 49
		11	47	- 54
6	14	8	56	+ 57

- Cont'd -

TABLE 2. (Cont'd.)

h	k	ℓ	$\|F_o\|$	F_c
6	14	10	21	- 7
6	16	8	23	+ 27
		10	21	+ 22
7	7	8	34	- 30
		10	19	+ 21
		12	19	+ 18
		14	19	- 21
		16	19	- 14
7	8	9	75	- 75
		13	82	+ 84
7	9	8	26	+ 34
7	11	10	52	- 52
7	12	11	19	- 18
		13	34	- 43
7	14	9	26	- 30
7	15	10	29	+ 24
8	8	8	56	+ 55
		10	52	+ 49
		12	19	- 23
8	9	9	48	- 53
		13	38	+ 36
8	11	11	21	- 32
8	13	11	21	- 25
8	16	8	42	+ 43

- Cont'd -

TABLE 2. (Cont'd.)

Unobserved terms used

in the least-squares refinement.

h	k	ℓ	$\|F_o\|$	F_c	h	k	ℓ	$\|F_o\|$	F_c
0	8	14	19	+17	3	4	13	20	+24
0	16	4	19	+19	3	4	15	19	-31
0	18	8	14	+37	3	7	12	20	+18
0	20	4	12	+29	3	9	10	20	+20
1	4	11	18	-20	3	13	6	20	+17
1	6	11	19	-15	3	15	4	19	+38
1	11	4	18	+17	4	9	13	19	-16
1	11	6	18	+16	5	9	10	20	+19
1	11	8	20	+22	5	9	12	19	-32
1	11	10	20	-16	5	13	8	19	-29
1	12	9	20	-29	6	9	11	20	+33
1	15	6	19	-16	6	12	8	19	+18
2	5	15	19	-30	7	10	9	20	+18
2	13	9	19	+25	9	9	10	19	-34
2	16	2	19	+19					

TABLE 5.

Sodium Hydrogen Diacetate:

Anisotropic Thermal Parameters.

($b_{ij} \times 10^5$)

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
Na(1)	228	228	228	-	-	-
Na(2)	268	268	268	-	-	-
O(1)	306	330	507	245	23	48
O(2)	279	248	675	-48	-184	65
C(1)	226	305	250	-157	-134	65
C(2)	273	632	571	89	445	-105

Atom	B‖x	B‖y	B‖z
Na(1)	1.60	1.60	1.60
Na(2)	1.88	1.88	1.88
O(1)	2.16	2.32	3.56
O(2)	1.96	1.74	4.74
C(1)	1.59	2.14	1.76
C(2)	1.92	4.44	4.01

TABLE 4.

Sodium Hydrogen Diacetate:

Final Atomic Coordinates and

Calculated Hydrogen Coordinates.

Coordinates are expressed as fractions of the cell edge (x, y and z). Origin is at centre of inversion occupied by Na(1).

Atom	x	y	z
Na(2)	0.11956	0.11956	0.11956
O(1)	0.03213	0.39144	0.09994
O(2)	0.07525	0.26521	0.13970
C(1)	0.08964	0.33971	0.11036
C(2)	0.17885	0.35908	0.08904
H(1)	0.204	0.402	0.136
H(2)	0.181	0.388	0.027
H(3)	0.215	0.301	0.089
H(4)	0.000	0.250	0.140

the centres of the atoms parallel to the (001) plane. Fig.VII consists of superimposed-contour sections of the atoms comprising the acetate group shown in Table 4 with the acetate group related by the two-fold axis $(0,\frac{1}{4},z)$ and the sodium ions. The electron-density map may be interpreted in terms of Fig.VIII which shows the basic acetate group in heavier lines with its immediate environment.

Atomic coordinates were calculated from the electron-density heights at a group of nine points in the neighbourhood of the atom by assuming that the electron density of an atom may be represented by

$$\log. \rho xy = k + ax^2 + by^2 + cx + dy + exy$$

and fitting the data at the nine points to this equation to give (x_o, y_o), the position of the maximum and ρ_o, the height of the maximum by the method of least-squares (cf. Shoemaker, Donohue, Schomaker and Corey, 1950). The coordinates obtained, shown in Table 5, are less reliable than those given by the least-squares refinement, as they involve termination-of-series errors.

The standard deviations of the atomic coordinates were derived from the least-squares residuals in the usual way and are given in Table 6.

The interatomic distances and bond angles, calculated from the final structure (Table 4), are listed in Table 7.

The standard deviations of bond length were calculated from the formula,

$$\sigma^2(d_{12}) = \sigma^2(x_1) + \sigma^2(x_2),$$

where $\sigma(x_1)$ and $\sigma(x_2)$ are the standard deviations of the atomic coordinates of the atoms participating in the bond, d_{12}, in the direction of the bond. When the atoms are related by a symmetry element, as in the case of the hydrogen bond, the equation becomes

$$\sigma(d_{12}) = 2\sigma(x_1).$$

The standard deviations of the bond angles were evaluated from

$$\sigma^2(\beta) = \sigma^2(A)/AB^2 + \sigma^2(B)\left\{1/AB^2 - 2\cos\beta/AB.BC + 1/BC^2\right\} + \sigma^2(C)/BC^2,$$

where β is the angle $A\text{-}\hat{B}\text{-}C$ and $\sigma(A)$, $\sigma(B)$ and $\sigma(C)$ are the standard deviations of the atoms A, B and C respectively (Cruickshank and Robertson, 1953). The estimated standard deviations are included in Table 7.

The atoms of the acetate group are coplanar and the equation of the plane through the four atoms is given by

$$0.1449\ X + 0.34179\ Y + 0.92860\ Z - 0.36826 = 0,$$

The maximum deviation from this plane is 0.004 Å in the case of atom C(1). The equation of the plane was calculated by the method of Schomaker et al. (1959).

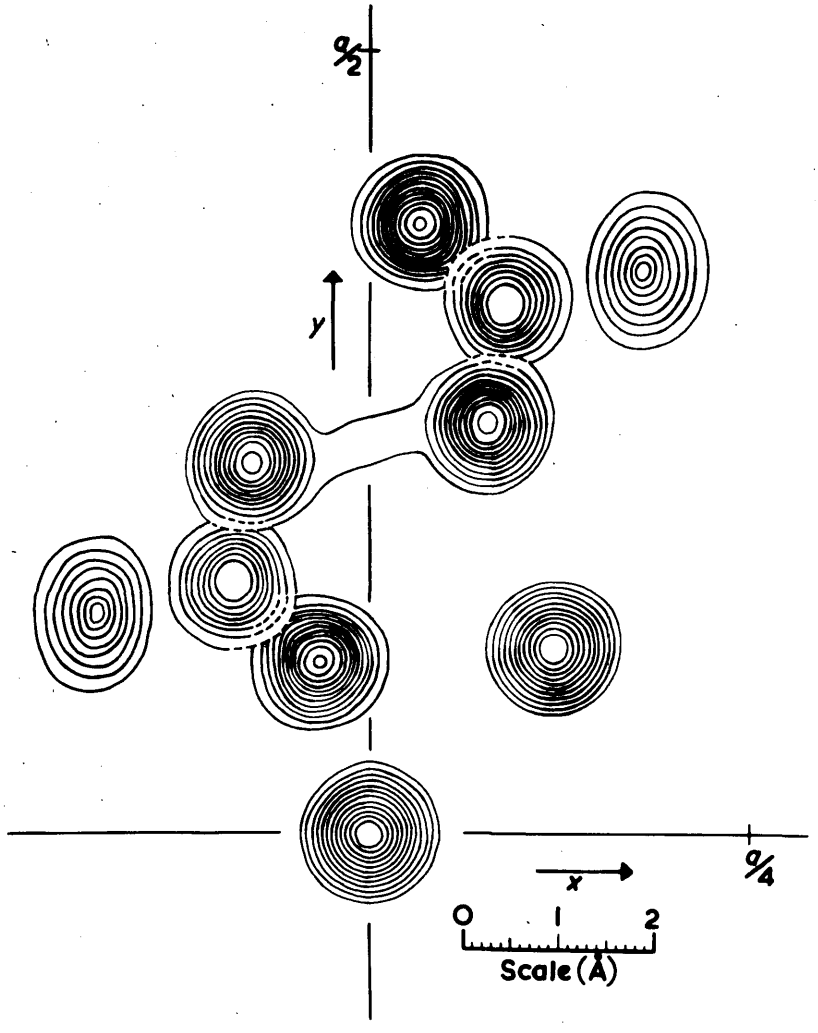


Fig.VII. Sodium Hydrogen Diacetate: Electron-density sections near the centres of the sodium, oxygen and carbon atoms. Contour-line interval: 1 electron per cubic Å, zero contour omitted; alternate lines round sodium ions are omitted.

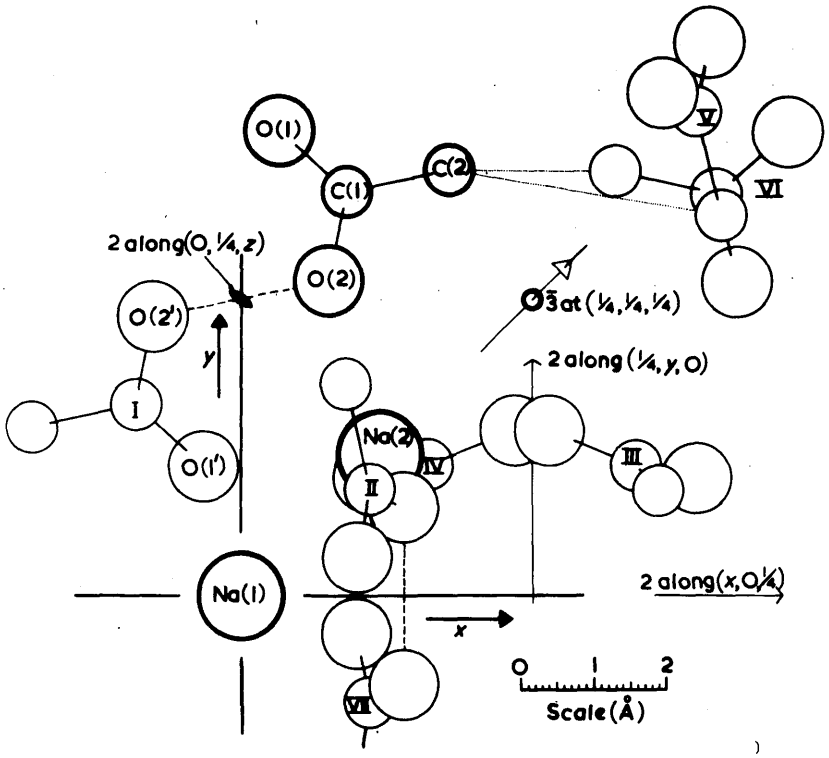


Fig.VIII. Sodium Hydrogen Diacetate: Projection of part of the structure, showing the "representative molecule" (drawn with heavier lines) and the following symmetry-related acetate groups: I ($\bar{x}$, $\frac{1}{2}$-y, z); II (z, x, y); III (y, z, x); IV ($\frac{1}{2}$-y, z, $\bar{x}$); V ($\frac{1}{2}$-z, $\frac{1}{2}$-x, $\frac{1}{2}$-y); VI ($\frac{1}{2}$-x, y, $\bar{z}$); VII (z, $\bar{x}$, $\frac{1}{2}$-y).
Hydrogen bonds are shown as broken lines; shorter intermolecular contacts as dotted lines.

TABLE 5.

Sodium Hydrogen Diacetate:

Atomic Coordinates from Fourier Synthesis.

Atom	x	y	z
Na(2)	0.1193	0.1193	0.1193
O(1)	0.0321	0.3906	0.0994
O(2)	0.0766	0.2630	0.1399
C(1)	0.0895	0.3405	0.1103
C(2)	0.1775	0.3601	0.0899

TABLE 6.

Sodium Hydrogen Diacetate:

Standard Deviations of the Final Atomic Coordinates (Å).

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Na(2)	0.0094	0.0094	0.0094
O(1)	0.0055	0.0058	0.0063
O(2)	0.0053	0.0053	0.0063
C(1)	0.0073	0.0082	0.0081
C(2)	0.0086	0.0108	0.0093

TABLE 7.

Sodium Hydrogen Diacetate:

Interatomic Distances and Bond Angles,

with their Estimated Standard Deviations in brackets.

Atoms	Distance
Na(1)...Na(2)	3.297 Å (0.016)
Na(1)...O(1)	2.404 (0.011)
Na(2)...O(1)	2.441 (0.011)
Na(2)...O(2)	2.445 (0.011)
O(2)...O(2)'	2.444 (0.010)
C(1) - O(1)	1.243 (0.010)
C(1) - O(2)	1.295 (0.010)
C(1) - C(2)	1.492 (0.012)

Atoms	Angle
O(1)-C(1)-O(2)	121.7° (0.7)
O(1)-C(1)-C(2)	122.3° (0.7)
O(2)-C(1)-C(2)	116.1° (0.7)
C(1)-O(2)...O(2)'	110.8° (0.5)

2.2.9. Description of the Structure.

The structure consists of 24 units of sodium hydrogen diacetate in a unit cell whose space group has equipoint 48. This means that the acidic hydrogen and the sodium ions occupy special positions. The analysis shows that the hydrogen atom is sited on a two-fold axis between two symmetry-related acetate groups to give the complex ion X..... H ..... X⁻ with axial symmetry (2). The sodium ions, on the other hand, are of two types. Ions of Na(1) are situated at the origin of the cell, (0,0,0), and the centre of the cell, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Two such sodium ions are about 14 Å apart and lie on the body-diagonal along which there is a three-fold axis. These positions correspond to centres of inversion, $\bar{3}$, on the three-fold axis and are 8-fold. The remaining sodium ions, type Na(2), are positioned on the three-fold axis to give triads of sodium ions Na(2) .... Na(1) .... Na(2) along the axes 3.29_7 Å apart. Three non-hydrogen-bonded oxygen atoms, type O(1) are arranged in a trigonal arrangement between Na(1) and Na(2) such that Na(1) is surrounded by six oxygen atoms of type O(1) at the corners of a regular trigonal antiprism. Na(2) is surrounded on one side by three atoms of O(1) and on the other side by three atoms of type O(2). These

six atoms are also arranged at the corners of a trigonal antiprism but this time it is irregular. This means that oxygen atoms from twelve different acetate residues make contact with any given triad.

In one acetate group, O(1) is bonded to sodium ions of both type whereas O(2) is bonded only to sodium ions of type 2 and these belong to different triads. The O(2) is hydrogen-bonded to another O(2) to give the complex ion X ... H ... X^-.

2.2.10. Discussion.

The most interesting intermolecular contact is the hydrogen bond joining O(2) atoms of the related acetate groups. It is apparently symmetrical and extremely short (2.444 ± 0.010 Å) and establishes sodium hydrogen diacetate as an acid salt of type A. The infrared spectrum of this compound which has been studied in detail by Hadzi and Novak (1960) supports this assignment.

The only other short intermolecular contacts occur between the methyl groups. They are arranged at the corners of a regular trigonal antiprism round the centre of symmetry at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and at a distance of about 3.3 Å from it. The distance between the carbon atoms of

methyl groups on one side of the centre is 3.834 Å. The other short non-bonded contact is between the carbon atoms of two methyl groups related by a two-fold axis, e.g. the "representative molecule" and VI in Fig.VIII; the distance, in this case, is 3.629 Å. These distances are shorter than the conventional van der Waals contact for methyl groups of 4.0 Å. The positions assigned to the hydrogen atoms of the methyl group show that the conformation about the C(1) - C(2) axis is such that the hydrogen atoms of one methyl group can pack into the slight cavity between the two hydrogens of the neighbouring group. This staggering of hydrogen atoms permits closer contacts between methyl groups than would otherwise be possible.

The average Na .... O bond length is 2.42 Å. The standard deviation for each individual bond length implies that no single value is significantly different from this average. The average is, however, greater than the sum of the crystal radii for oxygen and sodium given by Pauling (1960) of 2.35 Å. Although sixfold coordination of the sodium ion is quite common, the trigonal antiprism arrangement is unusual. The mean value obtained for this arrangement agrees with other values reported in the

literature for an octahedral arrangement. The following mean values have been determined : 2.438 Å in sodium bicarbonate, (Sass and Scheuerman , 1962); 2.46 and 2.44 Å for the two types of sodium ion in sodium sesquicarbonate (Brown, Peiser and Turner-Jones, 1949); 2.46 Å for sodium chlorate (Aravindakshan, 1959). Corbridge (1960) gives a table of Na .... O distances in ionic structures.

The bond lengths and angles in the carboxyl group are of considerable interest. Calculated distances for the C - O bond can be obtained from the equation 7.1 given by Pauling (1960),

$$D(A - B) = r_A + r_B - C\,|x_A - x_B|\,,$$

where r_A, r_B are the bond radii for the atoms A and B, $|x_A - x_B|$ is the difference in electronegativity of the two atoms and C is the Schomaker-Stevenson coefficient which has the value of 0.08 for all bonds involving first row atoms. If the values given by Pauling in Table 7.5 (1960) are used, the C - O double bond length and the C - O single bond length are theoretically predicted as 1.21 Å and 1.43 Å respectively.

In the completely ionised carboxylate group, the character of the C - O bond is mid-way between these extremes. Marsh (1958) has shown that in α-glycine

which exists as a zwitterion and hence has a completely ionised carboxylate group the C - O bond lengths are 1.265 and 1.261 Å. The two C - C - O bond angles are 117.4° and 117.1° and the O - C - O bond angle is 125.5°. In many carboxylic acids, the molecules occur as centro-symmetric dimers with hydrogen bonding between adjacent carboxyl groups. The C - (OH) and C - O distances in o-chlorobenzoic acid (Ferguson and Sim, 1960) are 1.295 and 1.208 Å and the angles C - C - O, C - C - (OH) and O - C - (OH) are 122.2°, 113.3° and 124.4° respectively. These results are fairly typical of this class of compound where the carboxylate group is unionised but slightly modified by hydrogen bonding.

In sodium hydrogen diacetate, an intermediate stage between the ionised and the unionised carboxylate groups is achieved. This is reflected in the bond lengths and angles obtained (Table 7). Cytosine-5-acetic acid (Marsh, Bierstedt and Eichhorn, 1962) forms two "symmetric" hydrogen bonds between pairs of equivalent atoms, oxygen in one case and nitrogen in the other, related to one another by centres of symmetry. This is explained in terms of the transfer of the proton from the acetic acid in one half of the molecules to a nitrogen atom in the

ring to give a zwitterion; the remaining half of the molecules are uncharged. The structure obtained in the analysis of cytosine-5-acetic acid is proposed as an average of the zwitterion and the uncharged state and has bond lengths and angles in the acetate group which would be expected to be similar to this acid salt. The bond lengths C - (OH) and C - O are 1.241 Å and 1.304 Å after correction for the libration implied by the temperature parameters and C - C - O, C - C - (OH) and O - C - (OH) bond angles are 120.6°, 116.1° and 123.3° respectively. These results agree excellently with the values in Table 7.

The C(1) - C(2) bond length is 1.492 ± 0.012 Å. This value differs, though not significantly, from the 1.54 ± 0.04 Å found in solid acetic acid (Jones and Templeton, 1958). It is in good agreement with the average value obtained by microwave spectra studies of acetyl derivatives of 1.499 Å (Krisher and Wilson, 1959 for references). The single bond distance between a carbon atom in the sp^2 state of hybridisation and a carbon atom in the sp^3 state of hybridisation has been estimated at 1.507 A (Dewar and Schmeising, 1959).

In α-glycine and cytosine-5-acetic acid, this bond has length 1.523 Å and 1.522 Å respectively.

SECTION 3. THE CRYSTAL STRUCTURE OF AMMONIUM HYDROGEN DICINNAMATE.

2.3.1. Introduction and Summary of Previous Work.

This acid salt, which was first reported by Carrick (1892), was the subject of an X-ray structural analysis in these laboratories by two-dimensional Fourier methods (Bryan, 1957). The results of this analysis establish quite clearly that ammonium hydrogen dicinnamate is an acid salt of type A. However, in projection the carboxyl groups overlap and there appears to be considerable and improbable distortion of the bond lengths and bond angles in this region.

The purpose of this study is to extend the data and use them in a partial three-dimensional refinement to determine if the bond lengths in this compound are significantly different from those found in similar compounds.

2.3.2. Experimental.

Ammonium hydrogen dicinnamate was prepared by mixing stoichiometric quantities of cinnamic acid in alcohol and concentrated ammonia. Crystals suitable for the X-ray investigation were obtained in the form of plates by

recrystallisation from 95% alcohol. The density of a freshly-prepared crystal, found by the method of flotation in carbon tetrachloride and dioxan was 1.25 which compares with the theoretical value of 1.240 and the value of 1.25 given by Bryan.

Crystals were mounted in two directions and these proved to be the b- and c- axes as chosen by Bryan. The intensities of the reflexions in the hk0, hk1, hk2, hk3, hk4 and hk5 nets were recorded using an equi-inclination Weissenberg camera; data for the h0ℓ, h1ℓ and h2ℓ nets were recorded using a normal-beam Weissenberg camera. These were supplemented at a later stage by observing the data about the b- axis on an equi-inclination Weissenberg camera. Cu Kα radiation was used.

The intensities were estimated visually using a "wedge" with spots of varying intensity on a known but relative scale and the multiple-film technique (Robertson, 1943). The intensity data were corrected for Lorentz and polarisation factors. The upper layer line data were also multiplied by the rotation factor appropriate to the method used in their collection (Cox and Shaw,1930; Tunell, 1939). The scale factor between each film in any one series was modified to allow for increased X-ray

path length through the film when upper zones are being collected (Rossmann, 1956).

As crystals of small and reasonably uniform cross-section were selected, no corrections were applied for absorption. Some 986 reflexions were observed in these nets out of 1972 accessible to Cu Kα radiation. The low percentage coverage is caused by the rapid fall-off in intensity; this is in agreement with the large temperature factors reported by Bryan. Of the above total of 986 reflexions, 687 independent reflexions were observed. The structure amplitudes, obtained from the usual formula for a mosaic crystal, are on a relative scale and were converted to an absolute scale by equating $\Sigma |F_o|$ and $\Sigma |F_c|$ for the reflexions of each net. The F_c values were calculated using the coordinates given by Bryan (Table 8) and an isotropic temperature factor of $B = 3$ Å^2 for all atoms. This resulted in scaling between nets which was inconsistent and hence further scaling was necessary. This was achieved by the method suggested by Dickerson (1959) and final scale factors were obtained which gave consistent results. This made available 687 reflexions on the same relative scale which closely approximated to the absolute scale.

2.3.3. Crystal Data.

The crystal data for ammonium hydrogen dicinnamate are given below:-

$NH_4H\ (C_8H_7COO)_2$. M = 313.34

Monoclinic prismatic a = 37.87 ± 0.12 Å

b = 5.84 ± 0.02 Å

c = 7.62 ± 0.03 Å

β = 95° 30' ± 1°

Volume of unit cell = 1677 $Å^3$.

ρ obs. = 1.25 ; calculated on the basis of four molecules per unit cell, ρ = 1.240.

F(000) = 664 .

Linear absorption coefficient for X-rays (λ = 1.5418 Å), μ = 8.39 $cm.^{-1}$

Absent spectra : (hkℓ) h + k + ℓ = 2n + 1.

(hOℓ) ℓ = 2n + 1 (h = 2n + 1).

(OkO) k = 2n + 1.

Space group : $I\ ^2/_a$ — C_{2h}^6 or Ia — C_s^4 .

2.3.4. Space Group.

It proved impossible to index the Weissenberg photographs in terms of the halving, h + k = 2n, implicit in the space group reported by Bryan. The photographs were successfully interpreted when the halving, h + k + ℓ = 2n, was assumed. This has the

effect of changing the space group from C 2/c or C c to I 2/a or I a.

Bryan selected the centrosymmetric space group on the evidence of intensity statistics and appears to have been justified by the successful outcome of his analysis. The space group used in this study was therefore I 2/a.

The space group I 2/a is, in fact, identical with C 2/c; they differ only in the choice of axes made to describe the unit cell. As C 2/c is listed in International Tables (1952), it is normally desirable to choose that orientation of axes which gives C 2/c. In this case it was decided to retain the choice of axes made by Bryan and accept the non-standard space group. The difference in the arrangement of the symmetry elements in the two systems can be seen in Figures X and XX, which show the unit cells of ammonium hydrogen dicinnamate with space group I 2/a and potassium hydrogen di-p-chlorobenzoate with space group C 2/c projected on to the (010) plane. I 2/a is based on a body-centred lattice. The equivalent positions are :

$$(0,0,0\ ;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}),\ \pm\ \left|\ x,y,z;\quad x,\bar{y},\tfrac{1}{2}+z\ \right|.$$

The structure factor expression for the space group is given by

$$A = 8 \cos 2\pi(hx + \ell z) \cos 2\pi ky$$

$$B = 0 ,$$

when ℓ is even,

and $A = -8 \sin 2\pi(hx + \ell z) \sin 2\pi ky$

$$B = 0 ,$$

when ℓ is odd.

(These expressions are identical with those derived for C2/c.)

The general expression for the electron density at any point (x y z) is

$$\rho(xyz) = \frac{4}{V_c}\left\{\sum_{h,k,\ell=0}^{\ell=2n}\sum\sum F(hk\ell) \cos 2\pi(hx + \ell z)\cos 2\pi ky - \sum_{h,k,\ell=0}^{\ell=2n+1}\sum\sum F(hk\ell) \sin 2\pi(hx + \ell z)\sin 2\pi ky\right\}.$$

At a later stage in this analysis, when the refinement was proceeding extremely slowly and it was felt that further confirmation of the choice of the centrosymmetric space group was required, intensity statistics were applied to the three-dimensional data now available. Two statistical tests were applied, the variance and N(z) tests.

In the variance test, which was first suggested by Wilson (1951), the average value for the square of the structure amplitudes of the reflexions in a range of

$\sin^2\theta$ is found, $\langle |F_o|^2 \rangle$. The mean square of the deviation of the square of the structure amplitude of each reflexion from the average value is calculated,

$$\langle \left| |F_o|^2 - \langle |F_o|^2 \rangle \right|^2 \rangle .$$

For a centrosymmetrical structure,

$$\langle \left| |F_o|^2 - \langle |F_o|^2 \rangle \right|^2 \rangle = 2 \langle |F_o|^2 \rangle \quad - 3a.$$

i.e. $\langle \left| |F_o|^2 - \langle |F_o|^2 \rangle \right|^2 \rangle \div \langle |F_o|^2 \rangle = 2,$

if a is assumed equal to zero.

For a non-centrosymmetrical structure

$$\langle \left| |F_o|^2 - \langle |F_o|^2 \rangle \right|^2 \rangle = \langle |F_o|^2 \rangle \quad - a.$$

If a is neglected, this becomes

$$\langle \left| |F_o|^2 - \langle |F_o|^2 \rangle \right|^2 \rangle \div \langle |F_o|^2 \rangle = 1.$$

It can be shown that a is $\sim \langle |F_o|^2 \rangle / N$, where N is the number of reflexions under consideration.

In the N(z) test, which was devised by Howells, Phillips and Rogers (1950), the intensities are again divided into ranges of $\sin^2\theta$ and values of $\langle |F_o|^2 \rangle$ found. The number of reflexions with values of $|F_o|^2$ equal to or less than 0.1 $\langle |F_o|^2 \rangle$ is calculated and expressed as a percentage of the total number of reflexions in the range, N(0.1). The percentage N(z) is thus found for z = 0.1 to z = 1.0.

As it is necessary to include all the reflexions in each range in these tests, the reflexions whose

intensities were not observable were noted and given a value for the intensity of half the minimum observed intensity for that net. These intensity data for the unobserved terms were processed in the same manner as the observed data. The squares of all the structure amplitudes were now formed and used as the data for the tests.

A STAC controlled program for DEUCE, devised by Dr. S.A.Sutherland, was available to perform these tests for four specified $\sin^2\theta$ ranges. The results are shown in Table 9. The predicted value of $N(z)$ for a centrosymmetrical and non-centrosymmetrical space group are also listed. The results indicate a centrosymmetrical distribution of intensities and support the choice of I 2/a as the space group.

2.3.5. Refinement of the Structure.

The structure was refined initially by three-dimensional Fourier methods and later by the least-squares method. An attempt to use the least-squares method immediately proved unsuccessful.

The numbering system used throughout this discussion is shown in Fig. IX. The oxygen involved in the hydrogen bond is O(1).

TABLE 8.

Ammonium Hydrogen Dicinnamate:

Final Atomic Coordinates obtained by Bryan.

Coordinates are referred to the monoclinic axes and are expressed as fractions of the axial lengths (x, y and z). Origin is at the centre of symmetry on glide plane c.

Atom	x	y	z
NH_4^+	0.000	0.5000	0.2500
O(1)	0.0280	0.1027	0.0543
O(2)	0.0470	-0.2700	0.0341
C(1)	0.0527	-0.0505	0.0730
C(2)	0.0902	-0.0476	0.1396
C(3)	0.1050	0.1490	0.1945
C(4)	0.1398	0.2124	0.2580
C(5)	0.1476	0.4181	0.3509
C(6)	0.1828	0.4698	0.4226
C(7)	0.2107	0.3091	0.4068
C(8)	0.2028	0.1132	0.3092
C(9)	0.1683	0.0604	0.2417

TABLE 9.

Ammonium Hydrogen Dicinnamate:

Intensity Statistics.

(A) Variance Test.

$\sin^2\theta$ Range.	No. of Reflexions.	Variance.
0.100 - 0.250	180	2.94
0.250 - 0.350	159	1.93
0.350 - 0.450	181	2.51
0.450 - 0.700	421	2.19

(B) N(z) Test.

Z	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Range											
1	0.0	27.6	40.8	48.0	52.9	55.7	58.5	61.2	65.1	66.2	68.2
2	0.0	21.0	35.6	40.5	52.8	57.8	64.0	65.2	67.7	68.3	68.3
3	0.0	22.9	34.5	45.4	55.8	60.7	65.1	66.2	67.8	68.9	70.9
4	0.0	23.7	36.8	42.3	50.9	59.8	62.7	65.5	67.8	69.4	70.2
$\bar{I}$	0.0	24.8	34.5	41.9	47.4	52.1	56.1	59.7	62.9	65.7	68.3
1	0.0	9.5	18.1	25.9	33.0	39.4	45.1	50.3	55.1	59.3	63.2

The final atomic coordinates given by Bryan were used as the initial structure; they are listed in Table 8. Structure factors were calculated for the 687 reflexions with temperature factors of $B = 4.4$ Å^2 for the oxygen atoms, $B = 5.5$ Å^2 for the carbon atoms and $B = 4.0$ Å^2 for the ammonium ion. At this stage the ammonium ion was treated as a simple nitrogen atom. As the ammonium ion is sited on a twofold axis of symmetry, the scattering curve for this ion is on half-scale. The value of R was 28.4%.

Two three-dimensional Fourier were summed. In the first, the observed structure amplitudes and the calculated phases were used as coefficients, a F_o synthesis; in the second, the structure factors were used as coefficients, a F_c synthesis. All the atoms were resolved and no spurious peaks appeared in the F_o map. The coordinates of the atoms were obtained from the electron-density heights of points in the neighbourhood of each peak by the method described by Booth (1948). The difference between the coordinates used in the structure-factor calculation and those obtained from the F_c synthesis gave the back-shift corrections caused by incomplete data and termination-of-series effects. These corrections were now applied to the coordinates from the F_o synthesis to give the improved structure.

The improved structure was used as the starting point for a further cycle of refinement. Two such cycles were completed and the value of R fell to 23.7%.

It was now apparent by comparing peak heights in the F_o and F_c maps that the temperature factors were not correct. Before any attempt was made to refine the thermal parameters, alterations were made to the scattering factors. The $O^{\frac{1}{2}-}$ curve derived from Freeman's results as discussed in section 2.2.5 was used. A scattering curve for the ammonium ion was obtained by starting the curve at $f = 10$ when $\sin\theta = 0$, approaching the normal nitrogen curve as $\sin\theta$ increases and joining it when $\sin\theta = 0.5$. The carbon and nitrogen scattering curves were taken from Berghuis et al. (1955).

Structure factors were calculated using the amended scattering curves and an isotropic temperature factor of $B = 5.5$ Å^2 for all the atoms. The R factor was now 21.7%.

A further cycle of refinement of positional parameters only reduced R to 21.1%. This small improvement indicated that the refinement of atomic coordinates using these methods was almost complete.

The method of applying back-shift corrections was modified. The atomic coordinates, calculated from a F_o synthesis, were used to give structure factors which were taken as coefficients in a F_c map. The differences between the coordinates from the F_o map and the F_c map gave the back-shift corrections and these were applied to the F_o map coordinates to give the improved structure. When this modified correction was applied to the results of the final cycle, the value of R improved to 21.0%.

Bond lengths for the final structure obtained by the Fourier refinement are given in Table 16. This Table also includes bond lengths calculated from Bryan's structure. The bond lengths in the carboxyl group show improvement and now agree with the expected values in that the C(1) - O(2) bond length is shorter than C(1) - O(1). The bond angles around C(1) remain anomalous. It was noticed in the refinement that the back-shift correction for C(1) was very large in the b- direction, 0.04 Å. This was three times larger than the corrections required for the other atoms. The double bond is shorter than the accepted value by 0.05 Å.

A (F_o - F_c) synthesis was computed and used to refine the thermal parameters. One cycle of refinement gave R = 19.5%.

The refinement was completed by the method of least-squares (Rollett, 1961); Table 10 summarizes the various stages in the refinement.

As the first attempt to use this method was unsuccessful and the structure now obtained did not give outstanding agreement between the observed and the calculated data, it was decided to refine, in the first instance, the parameters of the exocyclic atoms only. The anomalous dimensions are all contained in these atoms and an improvement in these atoms and an overall improvement in agreement would indicate the probability of the success of further refinement.

The general principles of the least squares method are discussed elsewhere. In this case, the value of F^{*} was 5.12 which is approximately equal to the average value of the observed amplitudes. At this stage of the refinement, the hydrogen atom contributions had not been included in the structure-factor calculation and as the compound is composed of "light" atoms only it would be expected that the hydrogen atoms would have a considerable effect. This effect is more important in the low-order terms, which have, in general, large structure amplitudes, than in the high-order terms which have small structure

TABLE 10.

Ammonium Hydrogen Dicinnamate:

Progress of Refinement by Least-Squares.

Phase	Cycle	R	$\Sigma w \Delta^2$	Notes.
1	1	19.5	-	$\sqrt{w_1}$ weighting system; exocyclic atoms only.
	2	18.3	-	
	3	17.8	119	
2	1	19.4	146	$\sqrt{w_1}$ weighting system; all atoms except NH_4.
	2	17.4	113	
	3	16.9	108	
	4	16.4	106	
	5	16.0	104	
3	1	16.2	51	$\sqrt{w_2}$ weighting system; hydrogen atoms in S.F. calculation.
	2	14.2	36	
4	1	16.2	48	Unobserved data included.
	2	14.2	38	
	3	13.7	30	
	4	13.5	29	
	5	13.4	-	

amplitudes. For this reason, it would be advantageous to weight the high-order terms and this is achieved by using the $\sqrt{w_1}$ weighting system.

Three cycles of refinement were computed and the results are shown in phase 1 of Table 10. The bond lengths were almost identical at the end of this phase with those at the end of the Fourier refinement and there was an improvement in the R factor. This can be attributed almost entirely to the thermal parameter changes. In particular, the results indicated very marked vibrations in the direction of the b- axis for C(1), C(2) and C(3). The refinement was now extended to all the atoms except the ammonium ion; the results are shown in Phase 2.

A $(F_o - F_c)$ synthesis was computed using the data provided by cycle 3 of phase 1. Peaks were observed in the regions expected to be occupied by hydrogen atoms. The coordinates of the hydrogen atoms were calculated assuming that the carbon to hydrogen bond length is 1.04 Å and the hydrogens are in the direction of the third bond of the sp^2 hybridised carbon atoms involved. Table 11 shows the numbering system used for the hydrogen atoms, the peak heights observed in the difference map and the calculated hydrogen coordinates.

TABLE 11.

Ammonium Hydrogen Dicinnamate:

Hydrogen Atoms.

(1) Bonded carbon atoms.

(2) Peak height in difference map (electrons A^{-3}.)

(3) Coordinates. See Table 13 for symbols.

Atom	(1)	(2)	x	y	z
H(1)	C(5)	0.40	0.127	0.517	0.369
H(2)	C(6)	0.30	0.187	0.617	0.492
H(3)	C(7)	0.40	0.236	0.355	0.454
H(4)	C(8)	0.40	0.224	0.004	0.293
H(5)	C(9)	0.44	0.165	-0.098	0.170
H(6)	C(2)	0.44	0.109	-0.175	0.146
H(7)	C(3)	0.49	0.087	0.282	0.182

The inclusion of the hydrogen atoms with a temperature factor of B = 8.0 $\AA^2$ in the structure-factor calculation reduced the R factor from 19.4% to 18.0%. The scattering curve calculated by McWeeny for the hydrogen atom was used.

Phase 3 of the refinement now proceeded. The $\sqrt{w_2}$ weighting system was used and the hydrogen atoms were included in the structure-factor calculation but were not refined. The final positional parameters and isotropic temperature factors obtained by averaging the temperature factors parallel to each axis calculated from the anisotropic data were used as the starting point.

In the final phase, those reflexions whose structure factor values implied that they should have been observable were included with a structure amplitude equal to half the local minimum observable. This meant that the final structure was weighted to lower the structure factors of these terms below the observable limit. As in the earlier stages of refinement, the bond length C(2) - C(3) was shorter than the theoretically predicted value and the position of C(2) was adjusted to make this bond length chemically more acceptable. A three-dimensional F_o map and $(F_o - F_c)$ map in the region of the ammonium ion were calculated and adjustments made to the y- coordinate and the isotropic temperature factor of this ion. This process was repeated after cycle 3 of Phase 4.

The final structure factors and the observed structure amplitudes for all reflexions used in the least-squares refinement are listed in Table 12. Although the structure factors were calculated on one-quarter scale throughout the analysis, this table shows full-scale values. The final value of R is 13.4% for the observed terms and 14.7% if the unobserved terms used in the refinement as described above are included.

2.3.6. Final Structure and Estimate of Accuracy.

The final atomic coordinates are given in Table 13; x, y, z are expressed as fractions of the crystallographic axes and X, Y, Z' are referred to the orthogonal axes $\underline{a}$, $\underline{b}$ and $\underline{c}^*$ and are measured in Angstrom units. These are obtained from the monoclinic axes by the transformation,

$$X = ax + cz \cos \beta ,$$

$$Y = by ,$$

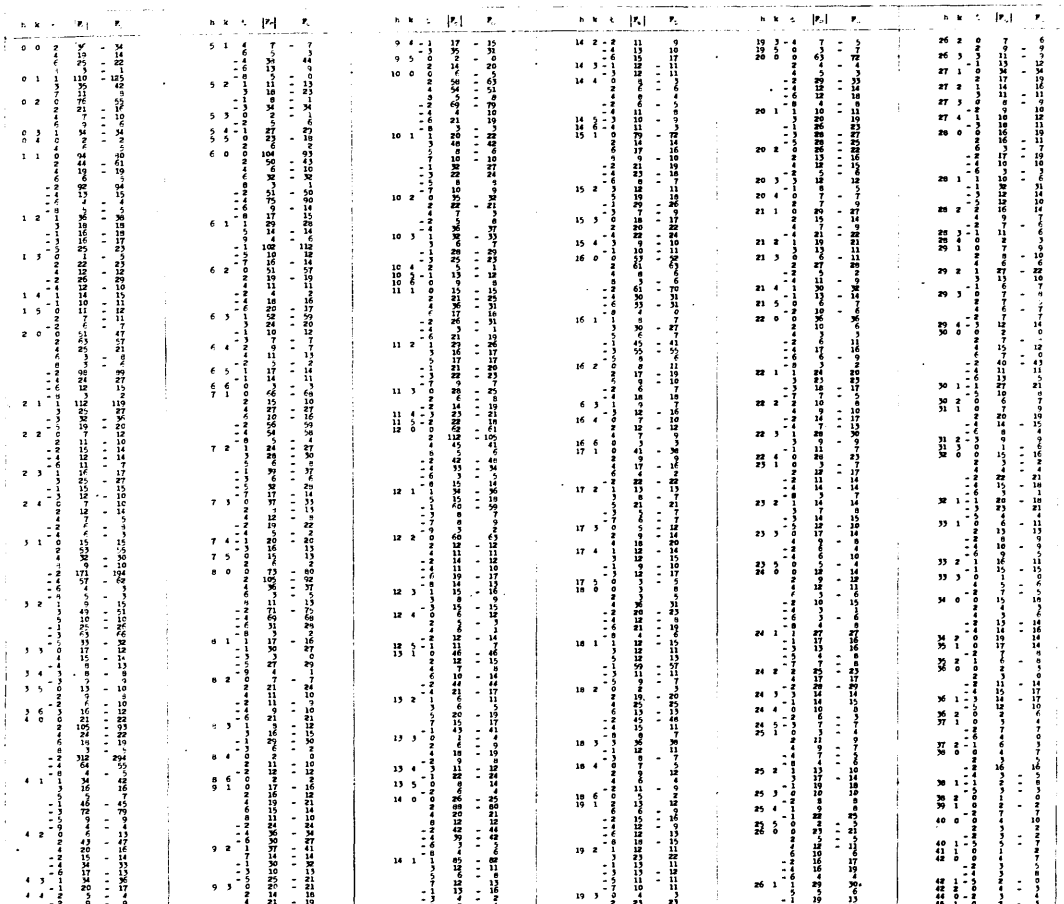
$$Z' = cz \sin \beta .$$

The final values of the anisotropic temperature parameters, given by the least-squares refinement, b_{ij}, are listed in Table 14. They are the parameters in the equation,

$$\exp - (B \sin^2\theta / \lambda^2) = 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + b_{12}hk + b_{23}k\ell + b_{31}\ell h)}.$$

TABLE 12.

Ammonium Hydrogen Dicinnamate.



Observed structure amplitudes and final calculated structure factors. The lower table gives the unobserved reflexions included in the least-squares refinement. In this case, the value of $|F_o|$ is the minimum locally observable.

TABLE 13.

Ammonium Hydrogen Dicinnamate:

Final Atomic Coordinates.

Coordinates x, y and z are expressed as fractions of the axial lengths and are referred to the monoclinic crystal axes. Coordinates X, Y and Z' are in Angstroms and are referred to the orthogonal system a, b and c^*. Origin as in Table 8.

Atom	x	y	z	X	Y	Z'
NH_4^+	0.0000	0.4747	0.2500	-0.183	2.772	1.896
O(1)	0.0302	0.0772	0.0509	1.105	0.451	0.386
O(2)	0.0466	-0.2849	0.0405	1.736	-1.664	0.307
C(1)	0.0531	-0.0837	0.0683	1.960	-0.489	0.518
C(2)	0.0921	-0.0404	0.1407	3.386	-0.236	1.067
C(3)	0.1034	0.1552	0.1895	3.776	0.906	1.438
C(4)	0.1414	0.2039	0.2616	5.165	1.191	1.984
C(5)	0.1480	0.4055	0.3540	5.348	2.368	2.685
C(6)	0.1821	0.4644	0.4233	6.585	2.712	3.211
C(7)	0.2099	0.3140	0.3995	7.657	1.834	3.030
C(8)	0.2033	0.1155	0.3098	7.474	0.675	2.350
C(9)	0.1694	0.0581	0.2380	6.242	0.339	1.805

TABLE 14.

Ammonium Hydrogen Dicinnamate:

Anisotropic Thermal Parameters.

($b_{ij} \times 10^5$).

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
NH_4^+	130	5497	3257	-	124	-
O(1)	160	6485	6346	-4042	351	-312
O(2)	121	8585	4333	- 592	127	- 97
C(1)	111	8763	3316	-1174	117	-467
C(2)	197	9297	3321	- 302	363	-677
C(3)	160	9865	2560	621	342	-1044
C(4)	129	7249	2200	1168	70	- 357
C(5)	134	6251	2965	645	198	- 46
C(6)	166	6000	2654	-	54	- 221
C(7)	133	7431	2682	- 29	50	- 410
C(8)	122	6308	2870	243	154	44
C(9)	126	6524	2200	- 212	135	- 383
H atoms	202	8458	5014	-	192	-

(B = 8.00)

TABLE 15.

Ammonium Hydrogen Dicinnamate:

Standard Deviations of the

Final Atomic Coordinates (Å).

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
O(1)	0.0070	0.0073	0.0076
O(2)	0.0058	0.0076	0.0068
C(1)	0.0085	0.0113	0.0092
C(2)	0.0107	0.0125	0.0095
C(3)	0.0097	0.0116	0.0090
C(4)	0.0091	0.0104	0.0082
C(5)	0.0092	0.0103	0.0091
C(6)	0.0095	0.0102	0.0084
C(7)	0.0089	0.0110	0.0089
C(8)	0.0086	0.0105	0.0087
C(9)	0.0086	0.0100	0.0081

TABLE 16.

Ammonium Hydrogen Dicinnamate:

Bond Lengths (Å).

(1) Final structure given by Bryan.

(2) Structure at end of refinement by Fourier methods.

(3) Final structure of this analysis. Estimated standard deviations in brackets.

Atoms	(1)	(2)	(3)	
O(1) - C(1)	1.29 Å	1.28 Å	1.277 Å	(0.012)
O(2) - C(1)	1.33	1.20	1.215	(0.012)
C(1) - C(2)	1.46	1.53	1.548	(0.015)
C(2) - C(3)	1.33	1.28	1.263	(0.015)
C(3) - C(4)	1.41	1.45	1.520	(0.014)
C(4) - C(5)	1.41	1.40	1.382	(0.013)
C(5) - C(6)	1.42	1.40	1.388	(0.013)
C(6) - C(7)	1.43	1.38	1.398	(0.013)
C(7) - C(8)	1.38	1.41	1.357	(0.014)
C(8) - C(9)	1.39	1.40	1.388	(0.013)
C(9) - C(4)	1.41	1.44	1.385	(0.013)
O(1)...O(1)'	2.51	-	2.509	(0.015)

TABLE 17.

Ammonium Hydrogen Dicinnamate:

Bond Angles.

(1) Final Structure given by Bryan.

(2) Structure at end of refinement by Fourier methods.

(3) Final structure of this analysis. Estimated standard deviations in brackets.

Atoms	(1)	(2)	(3)
O(1) - C(1) - O(2)	123°	126°	124.8°(1.0)
O(1) - C(1) - C(2)	134°	121°	122.2°(0.9)
O(2) - C(1) - C(2)	103°	113°	113.0°(0.9)
C(1) - C(2) - C(3)	119°	124°	122.5°(1.0)
C(2) - C(3) - C(4)	134°	125°	123.9°(1.0)
C(3) - C(4) - C(5)	123°	120°	117.6°(0.9)
C(4) - C(5) - C(6)	121°	124°	121.4°(0.9)
C(5) - C(6) - C(7)	120°	119°	118.6°(0.9)
C(6) - C(7) - C(8)	118°	120°	119.9°(0.9)
C(7) - C(8) - C(9)	122°	120°	121.6°(0.9)
C(8) - C(9) - C(4)	122°	120°	119.4°(0.9)
C(9) - C(4) - C(5)	117°		119.1°(0.9)
C(9) - C(4) - C(3)	120°		123.3°(0.9)
C(1) - O(1)...O(1)'	107°		110.0°(0.7)

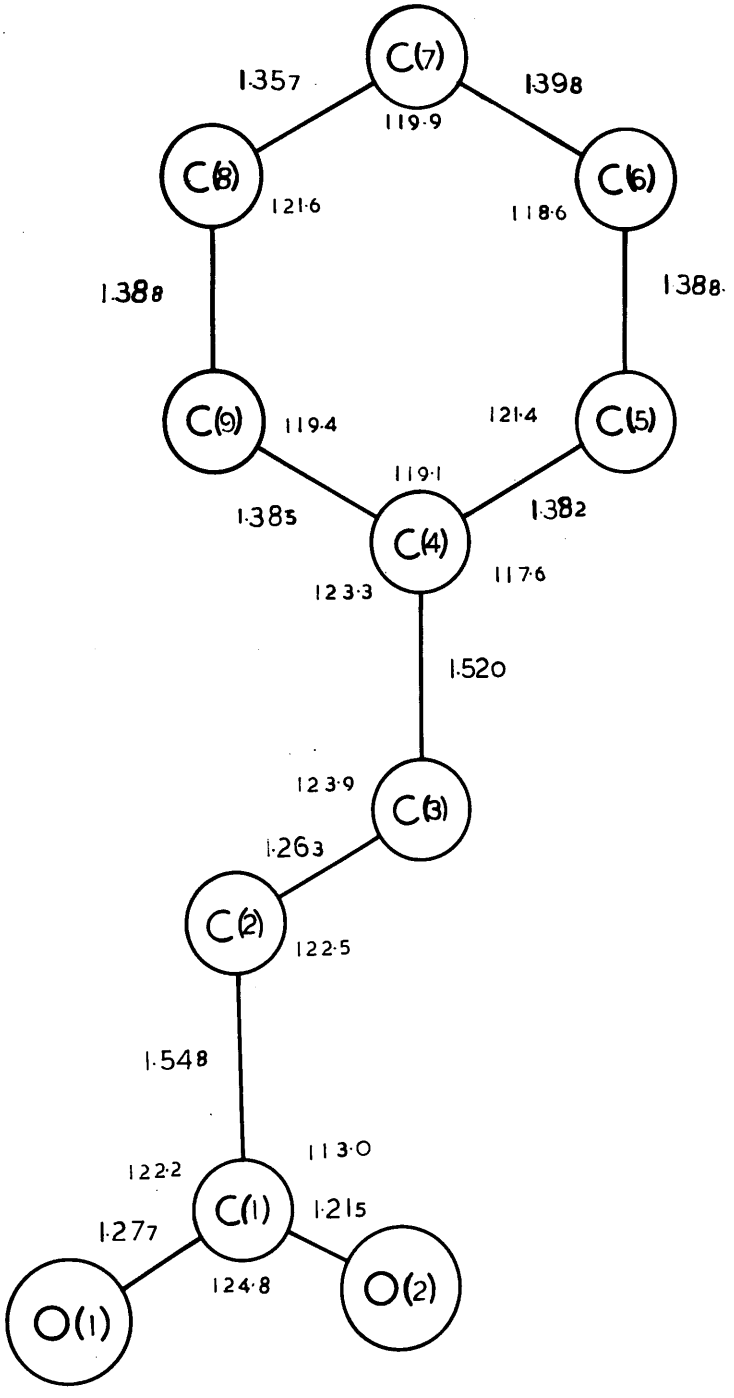


Fig. IX. Ammonium Hydrogen Dicinnamate: Interatomic distances (in Å) and valency angles.

The estimated standard deviations in atomic coordinates, calculated from the least-squares residuals, are given in Table 15.

2.3.7. Molecular Dimensions and Description of the Structure.

The bond lengths and bond angles calculated from the final coordinates (Table 13) are shown in Table 16, Table 17 and Fig.IX; these tables include the corresponding results for the structure obtained by Bryan and the structure obtained at the end of the Fourier refinement. Estimates of the standard deviations in bond lengths and bond angles, calculated by the formulae given in 2.2.8., are also given.

The plane through the carbon atoms of the benzene ring has the equation,

$$0.23760\ X + 0.46837\ Y - 0.85099\ Z' - 0.09866 = 0.$$

The mean planes were calculated by the method suggested by Schomaker et al (1959). This involves a least-squares minimisation of the perpendicular distances of the atoms from the plane. Application of the χ^2 test (Fisher and Yates, 1957) indicates that no atom deviates significantly from this plane for $\sum \Delta^2 = 1.31 \times 10^{-4}$, $\chi^2 = \sum \Delta^2/\sigma^2 = 1.03$ and $v = 6-3 = 3$.

The carbon atoms C(1), C(2), C(3) and C(4) lie on the plane,

$$0.32414\ X + 0.19019\ Y - 0.92669\ Z' - 0.06309 = 0.$$

The angle between this plane and the plane of the benzene ring is $17^{o}\ 18'$.

The atoms of the carboxyl and C(2) lie on the plane,

$$0.32022\ X + 0.13031\ Y - 0.93834\ Z' - 0.05785 = 0.$$

The angle between this plane and the plane of the benzene ring is $20^{o}\ 41'$.

Attempts to find other planes through groups of atoms, such that no atom of the group deviates significantly from the plane, failed. In particular, the mean plane through the exocyclic atoms and C(4) has $\sum \Delta^{2} = 2.69 \times 10^{-3}$. This leads to a value of $\chi^{2} = 26.9$ and $v = 6-3 = 3$ and means that deviations from the mean plane in this section of the molecule are significant.

Table 18 gives the perpendicular distances of the atoms of the cinnamate residue from the mean planes whose equations are given above.

The shorter intermolecular contacts are listed in Table 19, and the ammonium-oxygen distances are given in Table 20.

The structure is illustrated in Fig.X which shows the projection of half the unit cell on the (010) plane.

It consists of layers of cinnamate residues whose carboxyl groups are electrostatically bound to ammonium ions and which are hydrogen-bonded in pairs to form the dicinnamate groups characteristic of type A acid salts. The angle between the plane of the benzene ring and the (010) plane is 62°. The polar regions lie along the planes $x = 0$ and $x = \frac{1}{2}$ and the benzene rings are in contact at the twofold screw axes at $x = \frac{1}{4}$ and $x = \frac{3}{4}$. The ammonium ions are sited on the twofold axes. Each ammonium ion is surrounded by two sets of oxygen atoms which are both approximately tetrahedrally arranged. The oxygen atoms comprising the nearer set are all of type O(2) and the mean ammonium - oxygen distance is 2.89 Å. The second set are all of type O(1) and are 3.05 (x 2)Å and 3.59 (x 2)Å from the ammonium ion. Overall the eight oxygen atoms are in a very deformed cubic arrangement.

The equation of the plane through the carbon atoms of the benzene ring is given above. Fig.XI represents the three-dimensional electron-density distribution in this plane calculated by the method of Broadley et al (1959). The boundary lines h and g denote the intersections of this plane and the planes (100) and (010) respectively. To determine these axes it is necessary

to recalculate the equation of the plane with respect to the orthogonal axes $\underline{a}^*$, $\underline{b}$ and $\underline{c}$; the equation is

$$0.15499\ X' + 0.46837\ Y - 0.86983\ Z - 0.09866 = 0 ,$$

where X', Y and Z are in Angstrom unit and are related to the fractional coordinates by the equations,

$$X' = ax \sin \beta ,$$

$$Y = yb ,$$

$$Z = cz + xa \cos \beta .$$

The intersection of this plane and the plane $X' = 0$ (or 100) is the line,

$$- 0.86983\ Z = - 0.46837\ Y + 0.09886 .$$

If the angle between this line and the b- axis is θ, $\tan \theta$, the gradient of the line, is given by

$$\tan \theta = 0.46837/0.86983 = 0.5338.$$

$$\text{i.e. } \theta = 28^{\circ}\ 18' .$$

Similarly the angle (ϕ, say) between the a^*- axis and g is the gradient of the line,

$$- 0.86983\ Z = - 0.15499\ X' + 0.09886 .$$

$$\text{i.e. } \tan \phi = 0.1782$$

$$\text{i.e. } \phi = 10^{\circ}\ 6' .$$

The lengths of the lines h and g are :

$$h = b/\cos 28^{\circ}\ 18' = 6.63\ \text{Å} ,$$

$$g = a \sin \beta/\cos 10^{\circ}\ 6' = 38.29\ \text{Å} .$$

TABLE 18.

Ammonium Hydrogen Dicinnamate:

Deviations from the Mean Planes.

(a) Plane through the benzene ring atoms C(4),.....,C(9).

(b) Plane through C(1), C(2), C(3) and C(4).

(c) Plane through O(1), O(2), C(1) and C(2).

Atom	(a)	(b)	(c)
O(1)			-0.007
O(2)			-0.007
C(1)		-0.001	+0.020
C(2)		+0.001	-0.005
C(3)		+0.001	
C(4)	-0.002	-0.001	
C(5)	-0.004		
C(6)	+0.004		
C(7)	+0.001		
C(8)	-0.007		
C(9)	+0.007		

TABLE 19.

Ammonium Hydrogen Dicinnamate:

Intermolecular Distances < 4 Å.

Atoms	Distance	Atoms	Distance
O(1)...O(1)^{I}	3.92 Å	C(9)...C(9)^{I}	3.87 Å
O(1)...O(2)^{I}	3.92	C(7)...C(8)^{II}	3.81
O(1)...C(1)^{I}	3.96	O(1)...O(1)^{III}	2.51
C(1)...O(1)^{I}	3.86	O(1)...O(2)^{III}	3.17
C(1)...C(1)^{I}	3.93	O(1)...C(1)^{III}	3.20
C(2)...C(1)^{I}	3.78	O(1)...O(1)^{IV}	3.97
C(2)...C(2)^{I}	3.84	O(1)...O(2)^{V}	3.78
C(3)...O(2)^{I}	3.67	C(5)...C(4)^{VI}	3.88
C(3)...C(1)^{I}	3.63	C(5)...C(5)^{VI}	3.97
C(3)...C(2)^{I}	3.57	C(6)...C(4)^{VI}	3.68
C(4)...C(2)^{I}	3.71	C(6)...C(5)^{VI}	3.72
C(4)...C(9)^{I}	3.99	C(6)...C(6)^{VI}	3.83
C(5)...C(2)^{I}	3.83	C(6)...C(7)^{VI}	3.90
C(6)...C(9)^{I}	3.94	C(6)...C(8)^{VI}	3.86
C(7)...C(9)^{I}	3.81	C(6)...C(9)^{VI}	3.74
C(8)...C(9)^{I}	3.76		

TABLE 20.

Ammonium Hydrogen Dicinnamate:

Ammonium Ion - Oxygen Distances (Å).

Atoms	Distance.
$NH_4....O(1)$	3.054 Å
$NH_4....O(2)^{I}$	2.914
$NH_4....O(2)^{III}$	2.914
$NH_4....O(1)^{IV}$	3.054
$NH_4....O(2)^{V}$	2.859
$NH_4....O(1)^{VI}$	3.593
$NH_4....O(1)^{VII}$	3.593
$NH_4....O(2)^{VIII}$	2.859

In Tables 19 and 20, the superscripts refer to the following positions:

I	$x, \bar{y}, \frac{1}{2}+z$	V	$x, 1+y, z$
II	$\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$	VI	$x, 1-y, \frac{1}{2}+z$
III	$\bar{x}, \bar{y}, \bar{z}$	VII	$\bar{x}, 1-y, \bar{z}$
IV	$\bar{x}, y, \frac{1}{2}-z$	VIII	$\bar{x}, 1+y, \frac{1}{2}-z$

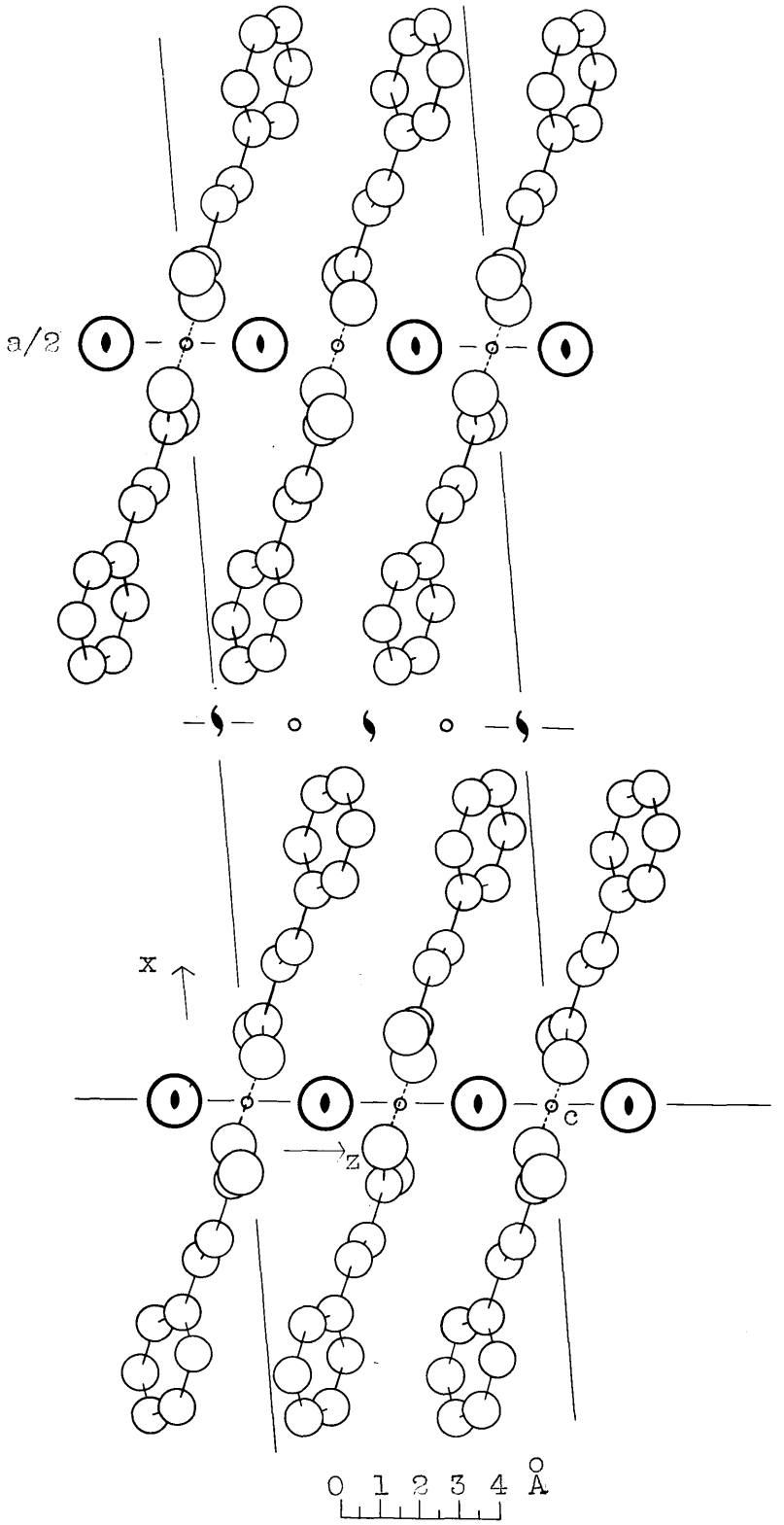


Fig.X. Ammonium Hydrogen Dicinnamate: Projection of part of structure on (010). Ammonium ions are drawn with heavier lines; hydrogen bonds are shown as broken lines.

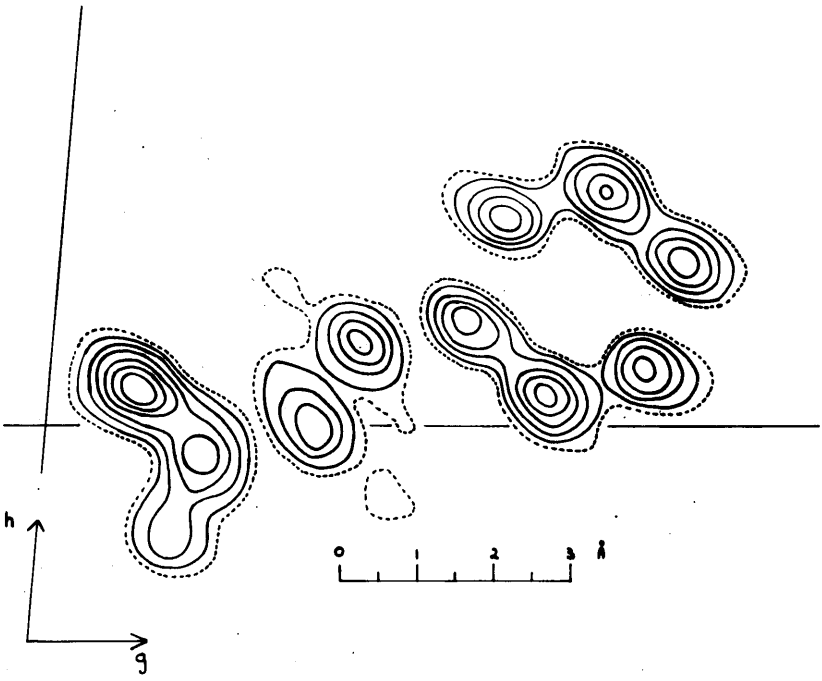


Fig. XI. Ammonium Hydrogen Dicinnamate: Electron-density section in the plane of the carbon atoms of the benzene ring. The exocyclic atoms are out of this plane. Contour-line interval: 1 electron per cubic Å with 0.5 electron contour shown as broken line.

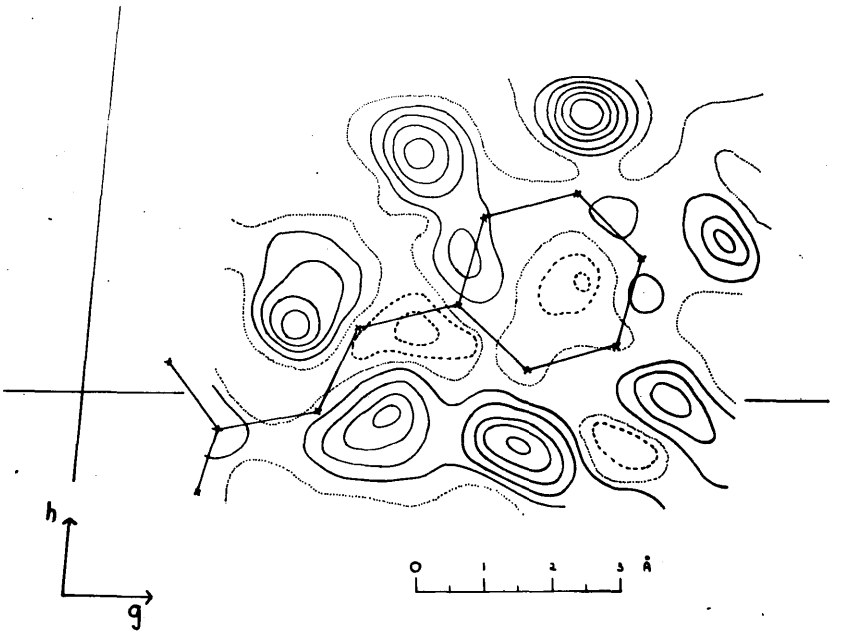


Fig.XII. Ammonium Hydrogen Dicinnamate; Difference-synthesis in the plane of the carbon atoms of the benzene ring to show the hydrogen atoms. Contour-line interval: 0.1 electrons per cubic Å, zero contour drawn as dotted line and negative contours as broken lines.

The angle between h and g is

$$\cos^{-1}(\sin 28^{\circ}5' \times \sin 10^{\circ}6')$$

i.e. $85^{\circ}16'$

A triple $(F_o - F_{c'})$ synthesis was also computed. Here $F_{c'}$ is the calculated value of the structure factor for the carbon and oxygen atoms alone.. In the resulting map, which is shown in Fig.XII the hydrogen atoms appear as well-resolved peaks.

2.3.8.. Discussion.

As in other acid salts of Type A, the two cinnamate residues are crystallographically indistinguishable being related by a centre of symmetry. They are joined by a short hydrogen bond of length 2.509 ± 0.015 Å. The angle C(1) - O(1) .... O(1)' is very close to tetrahedral (110°); this value is the most favourable for the formation of a strong hydrogen bond (Fuller, 1959).

The average C - C bond length in the benzene ring is 1.383 Å. Although this is less than the literature value of 1.395 Å (Tables of Interatomic Distances, 1958), the individual bond lengths in the benzene ring do not deviate significantly from this mean value. The bond angles in the benzene ring require no comment.

The most unexpected feature of the analysis is the length of the exocyclic double bond, C(2) - C(3). It has length 1.263 Å which is considerably less than the accepted value for a double bond, 1.337 Å (Tables of Interatomic Distances, 1958). This bond length cannot be accepted from a chemical standpoint and there are three reasons which may account for the difference. First, the standard deviations may have been underestimated by at least 50%; secondly, errors in the intensity data may have resulted in wrong carbon atom positions; thirdly, the structure is subtly disordered and some account of this ought to have been made. It is significant that the temperature factors of the exocyclic atoms suggest that these atoms are undergoing highly anisotropic vibrations and that the direction of greatest amplitude is in the direction of the b- axis, along which any movement would greatly affect the length of the double bond.

The bond lengths of the carboxylate group require no comment (cf. 2.2.10). The bond angles, however, are anomalous; it is expected that C(2) - C(1) - O(1) would approach the tetrahedral angle more closely than C(2) - C(1) - O(2), whereas, in this case, the reverse arrangement is observed. From Table 18, it can be seen that C(1) deviates from the best plane through O(1), O(2),

C(1) and C(2) by 0.02 Å. Application of the χ^2 test to this plane shows that as $\Sigma\Delta^2 = 5.3 \times 10^{-4}$, $\sigma^2 = 9.5 \times 10^{-5}$, $\chi^2 = 5.57$ and $v = 4-3 = 1$, $p = 0.02$. This indicates that it is possible that C(1) deviates significantly from this plane. During the Fourier refinement, it was noticed that C(1) required a large back-shift correction. The C(1) - C(2) bond length is longer than that expected in unsaturated carboxylic acids.

Dewar and Schmeising (1959) predict that the C - C single bond length between sp^2 hybridised carbon atoms is 1.471 Å. This bond has been found to be 1.45 Å in sorbic acid (Sutherland, 1961), 1.46 Å in β-ionylidene crotonic acid (Eichhorn and MacGillavry, 1959), 1.50 Å in crotonic acid (Sutherland, 1961) and 1.46 Å in tiglic acid (Porte and Robertson, 1959). To sum up, it would appear that the positions of C(1) and C(2) are in error in some way for small shifts of the same order as the back-shift correction applied to C(1) and C(2) would correct all these anomalies.

The deviation from overall planarity is probably caused by the steric repulsion of the hydrogen atoms at C(2) and C(9). This repulsion could also account for the observed bond angles around C(4) and C(3); this

assumes that the deviation of these angles from 120° is to be treated as significent in view of the discussion given above.

The arrangement of the eight oxygen atoms round the ammonium ion is of considerable interest. The four nearest neighbours are oxygen atoms of type O(2) at a mean distance of 2.89 Å. (See Table 20). This distance is characteristic of that in many crystals containing NH_3^+.....COO^- bonds; the mean distance for such bonds is 2.83 ± 0.08 Å (Fuller, 1959). In ammonium oxalate monohydrate (Hendricks and Jefferson, 1936; Jeffrey and Parry, 1952), the ammonium ion is tetrahedrally surrounded by two sets of oxygen atoms and the mean NH_4^+ ..... O^- distances are 2.80 Å and 3.20 Å. A neutron - diffraction study of tetragonal ammonium dihydrogen phosphate (Tenzer, Frazer and Pepinsky, 1958) has revealed that the ammonium ion is surrounded by eight oxygen atoms, four of which are involved in hydrogen bonds of length 2.92 Å; the remaining four oxygen atoms are at a distance of 3.17 Å. Gillespie, Sparks and Trueblood (1959) have shown that in ammonium chlorite, each ion is tetrahedrally surrounded by four oxygen atoms at a distance of 2.83 ± 0.03 Å. In ammonium tetrametaphosphate (Romers, Ketelaar and

MacGillavry, 1951), the four nearest neighbours of each of the ammonium ions are again tetrahedrally arranged at a similar distance with other oxygen atoms about 0.3 Å farther away. Ammonium hydrogen phthalate (Okaya and Pepinsky, 1957) and ammonium hydrogen disalicylate hydrate (Downie and Speakman, 1954) contain ammonium ions which are six-coordinated; the mean $NH_4^+ \ldots\ldots O^-$ distances are 2.94 Å and 2.91 Å respectively.

In ammonium hydrogen dicinnamate, the surroundings of the ammonium ion indicate the possibility of the presence of hydrogen bonding, N - H .... O. This implies that the hydrogen atoms of the ammonium ion are ordered. On the other hand, Waddington (1958) has suggested, on the evidence of a careful study of the infrared spectra of some ammonium salts of monobasic acids, that, in those ammonium salts which are isomorphous with the corresponding rubidium and potassium salts, the ammonium ion is free to rotate. As, in this case, potassium and ammonium hydrogen dicinnamates are isomorphous, it has been assumed that the hydrogen atoms of the ammonium ion are disordered. This assumption means that, in deriving the ammonium ion scattering curve, a good approximation is achieved by treating the ion as

a freely rotating group. Jeffrey and Parry (1952) have described a scattering curve calculated on this basis and it differs from the scattering curve used in this refinement (cf. 2.3.5) in that it approaches the normal nitrogen curve at $\sin\Theta = 0.35$ and falls below it as Θ further increases to become identical at $\sin\Theta = 0.79$ and beyond.

All the atoms in the structure have very large thermal parameters. These are not confined, as would be expected, to the carbon atoms which are linked by relatively weak van der Waals attraction but are present in the oxygen atoms which are electrostatically and hydrogen bonded. It is interesting to note that Ladell, McDonald and Schmidt (1956, 1957) obtained very poor resolution in their study of α-trans cinnamic acid when the data were collected at room temperature.

SECTION 4: THE CRYSTAL STRUCTURE OF SOME ACID SALTS OF p-CHLOROBENZOIC ACID.

2.4.1. Introduction.

Recently, Shrivastava and Speakman (1961) have shown that the potassium acid salts of o-nitrobenzoic and p-nitrobenzoic acids belong to type A and type B acid salts respectively.

The only other para-substituted acid salt whose structure has been determined is potassium hydrogen di-p-hydroxybenzoate; this salt is hydrated and exhibits hydrogen bonding between the hydroxyl groups and the molecules of water of crystallisation (Skinner and Speakman, 1951). It thus seemed logical to study an acid salt which is para- substituted but does not have hydrogen bonding between neighbouring para- substituents to see if the type is related to the position of the substituent. For this purpose, p-chlorobenzoic acid was chosen as its acid salts were known having been the subject of an investigation of thermodynamical properties of acid salts by Smith (1949).

A preliminary examination of the X-ray photographs of the rubidium, potassium and ammonium salts established

that these salts are isotypic and, in the case of the first two, isomorphous. That the ammonium salt is also isomorphous was not obvious from the X-ray photographs but was established in the course of the analysis.

The structure of the rubidium salt in the most favourable projection was found and this structure was used as the trial model in the interpretation of this projection of the other two salts. A second projection of the potassium salt was solved and a partial three-dimensional refinement of the potassium salt completed the analysis.

2.4.2. Infrared Spectrum.

The infrared spectra of p-chlorobenzoic acid and some salts of p-chlorobenzoic acid are shown in Fig.XIII. In this discussion, the wave numbers quoted for the bands are of qualitative, rather than quantitative, significance. All the infrared spectra were taken with the solids mulled in nujol and hence show the absorption bands characteristic of nujol, viz. 2900 $cm.^{-1}$ (C - H stretching) and 1460 $cm.^{-1}$ (C - H deformation). In all five spectra, the following bands are common and have been assigned as follows (Bellamy, 1958) : 850 $cm.^{-1}$ is characteristic of 1:4 dibenzene derivatives, the band at 1100 $cm.^{-1}$ is

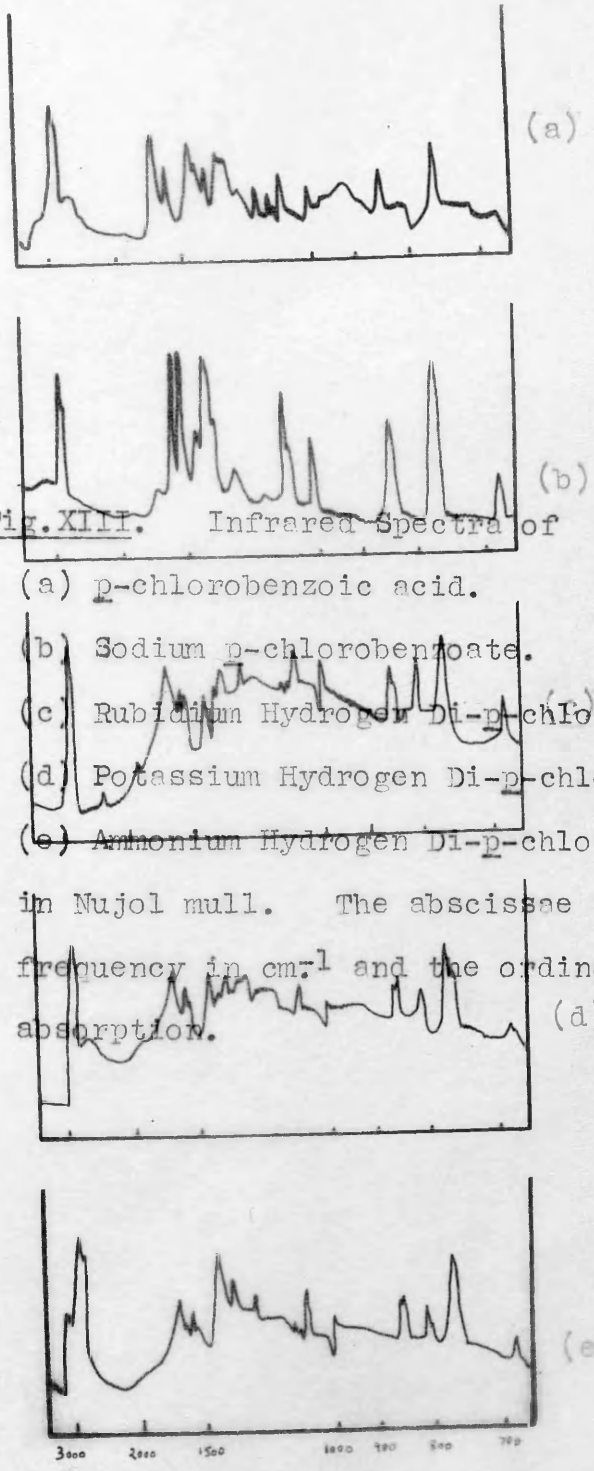


Fig.XIII. Infrared Spectra of

(a) p-chlorobenzoic acid.

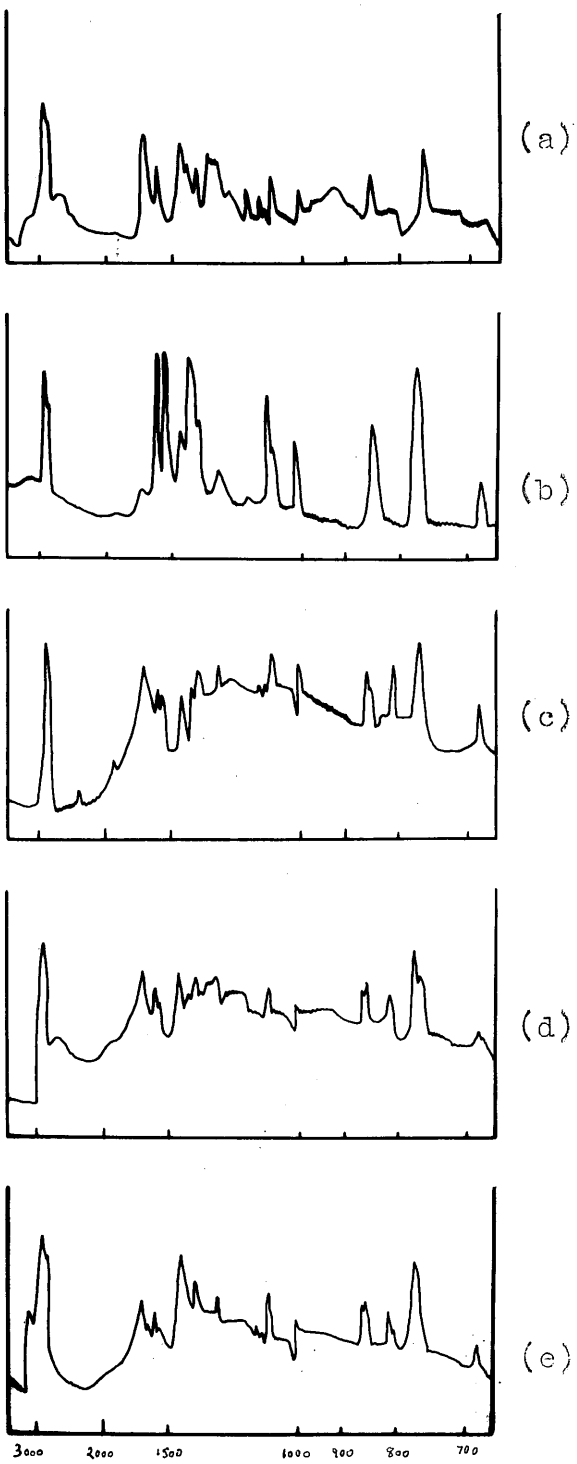
(b) Sodium p-chlorobenzoate.

(c) Rubidium Hydrogen Di-p-chlorobenzoate.

(d) Potassium Hydrogen Di-p-chlorobenzoate.

(e) Ammonium Hydrogen Di-p-chlorobenzoate.

in Nujol mull. The abscissae represent the frequency in $cm.^{-1}$ and the ordinates show absorption.


(a)
(b)
(c)
(d)
(e)
3000
2000
1500
1000
900
800
700

attributable to C - Cl deformation (Katritzky and Lagowski, 1960), the band at 774 $cm.^{-1}$ to C - Cl (stretching) and the band at 1590 $cm.^{-1}$ to aromatic C - C vibrations.

In the spectrum of p-chlorobenzoic acid, the features characteristic of carboxylic acids which exist in dimeric form with strong hydrogen bonding between the carbonyl and hydroxyl groups of neighbouring molecules are present (Bellamy, 1958). These are bands at 2700 - 2400 $cm.^{-1}$ (O - H stretching), 1680 $cm.^{-1}$ (C = O vibration in aryl acid), 1420 $cm.^{-1}$, 1320-1280 $cm.^{-1}$ and 950-900 $cm.^{-1}$ (O - H deformation). In sodium p-chlorobenzoate, the COO^- group is present and resonance is possible between the two C - O bonds. In consequence, the characteristic carbonyl absorption has vanished and is replaced by two bands at 1545 $cm.^{-1}$ and 1420-1380 $cm.^{-1}$, which corresponds to the antisymmetric and symmetric vibration of the COO^- structure.

The spectra of the acid salts are not a simple superposition of the spectra described above but are dominated by the extremely broad band of absorption below 1400 $cm.^{-1}$. This is characteristic of type A acid salts and the assignments which follow have been

made by comparison with the work of Hadzi and Novak (1960) on type A acid salts. There is a broad band of absorption near 1680 $cm.^{-1}$ which is attributable to strong C = O and O - H stretching vibrations. The broad band is assigned to deformation modes of COOHOOC groups. There is no peak above 1680 $cm.^{-1}$ which could be attributed to O - H stretching and the band at 950 $cm.^{-1}$ in the free acid is not identifiable.

Thus, prior to the X-ray investigation, we predicted that the acid salts of p-chlorobenzoic acid belong to type A.

RUBIDIUM HYDROGEN DI-p-CHLOROBENZOATE.

2.4.3. Experimental.

Rubidium hydrogen di-p-chlorobenzoate was prepared by mixing alcoholic solutions of one equivalent of rubidium carbonate and two equivalents of p-chlorobenzoic acid. The acid salt separated from the mother liquor and crystals suitable for X-ray purposes were obtained by recrystallisation from 95% alcohol. These consist of plates elongated in the direction of the b- axis. The density was determined by the method of flotation in a chloroform/bromoform mixture.

The unit cell dimensions and space group were obtained from rotation, oscillation and Weissenberg photographs about the a- and c- axes.

The intensities of the $h0\ell$ reflexions were recorded on Weissenberg photographs, using Cu Kα radiation, and estimated visually using the multiple-film technique (Robertson, 1963). All intensities were corrected by application of the Lorentz and polarisation factors to give a table of relative structure amplitudes. The absolute scale was established later by correlating the observed amplitudes with the calculated structure factors.

Although the absorption coefficient is large, no absorption corrections were applied as it was not intended to use the data in a refinement of the structure. Some 141 intensity data were observed.

2.4.4. Crystal Data.

The crystal data for rubidium hydrogen di-p-chlorobenzoate are given below :-

$RbH(ClC_7O_2H_4)_2$ M = 397.58

Monoclinic a = 33.2 ± 0.2 Å.

b = 3.89 ± 0.04 Å.

c = 11.47 ± 0.10 Å.

$\beta = 92.1^\circ \pm 1^\circ$

Volume of the unit cell = 1480 $Å^3$.

$\rho_{obs.} = 1.79$; $\rho_{calc.}$ (with z = 4) = 1.78_4.

F(000) = 784.

Linear absorption coefficient for X-rays ($\lambda = 1.542$ Å), $\mu = 82.6\ cm.^{-1}$.

Absent Spectra : (hkℓ) h + k = 2n + 1

(hOℓ) ℓ = 2n + 1

(OkO) k = 2n + 1

Space Group : C 2/c — C_{2h}^6 or C c — C_s^4

2.4.5. Space Group.

From experience gained in the structural studies of other acid salts (2.3.4.), the space group was assumed to be C $2/c$. This choice has been justified by the successful outcome of the analysis.

This space group provides eight equivalent positions. Since there are four molecules of $RbH(ClC_7O_2H_4)_2$ in the unit cell, the rubidium ions and the acidic hydrogen atoms must occupy special positions, in this case either a centre of symmetry or a twofold axis of symmetry. This implies that the p-chlorobenzoate residues must also be related by either a centre of symmetry or a twofold axis.

2.4.6. Determination of Atomic Positions in the (010) Projection.

The h0ℓ data were used to compute the Patterson function for the (010) projection, P(uw), which is given by

$$P(uw) = \frac{1}{A} \sum \sum |F(h0\ell)|^2 \cos 2\pi(hu + \ell w),$$

where A is the area of the projection.

The plane group of this projection is p2 and the rubidium ions project on to a centre of symmetry which can be

taken as the origin. This greatly facilitated the interpretation of the Patterson map as the most prominent peaks correspond to vectors between the rubidium ion and each of the other atoms in turn; vectors between the "lighter atoms", chlorine, carbon and oxygen give very much smaller peaks, the height of the peak being proportional to the product of the atomic numbers of the atoms giving the vector represented by the peak. The Patterson map gives peaks corresponding to vectors between each atom and the rubidium ion in the position occupied by that atom in the corresponding electron-density map of the projection. The Patterson map is illustrated in Fig.XIV.

The rubidium ion will be expected to be phase-determining; structure factors calculated with the origin taken at the rubidium ion are, in fact, mostly positive. (In Table 23(a), the origin is no longer at the rubidium ion and this simple rule of all positive phases breaks down.)

This means that the Patterson function corresponds to a distorted electron-density summation in that most of the coefficients have the correct phases but the square of the structure amplitude is used in place of the structure amplitude.

From the Patterson map, atomic positions for all the atoms were derived from the peaks using Booth's method; these coordinates are shown in Table 21.

The numbering system used in this discussion to describe the p-chlorobenzoate group is shown in Fig.XIX; O(1) is involved in the hydrogen bond.

2.4.7. Refinement of the (010) Projection.

Structure factors were calculated with the atomic coordinates obtained from the Patterson projection. All the atoms were assigned a temperature factor (B) of 3.0 $\AA^2$; the scattering factors for rubidium, chlorine, oxygen and carbon were taken from Berghuis et al. (1955). The rubidium scattering curve was on half-scale. Structure factors calculated for the rubidium ion and the chlorine atom gave an R factor of 39%. The inclusion of all the atoms in the calculation reduced this to 21%.

The value of R indicates that the structure is basically correct and an electron-density map computed using the observed structure amplitudes and the calculated phases was satisfactory. As, in this projection, the atoms are all perfectly resolved it is permissible to use the

method of least squares for further refinement (Srinivisan, 1961). After six cycles, the R factor was reduced to 15%. The weighting system used was $\sqrt{w_2}$ with F^* equal to 12.80.

The final atomic coordinates with averaged isotropic temperature factor are shown in Table 22; the origin is taken at the centre of symmetry as in International Tables (1952). The values of the observed structure amplitudes and the final calculated structure factors are listed in Table 23(a) on full-scale.

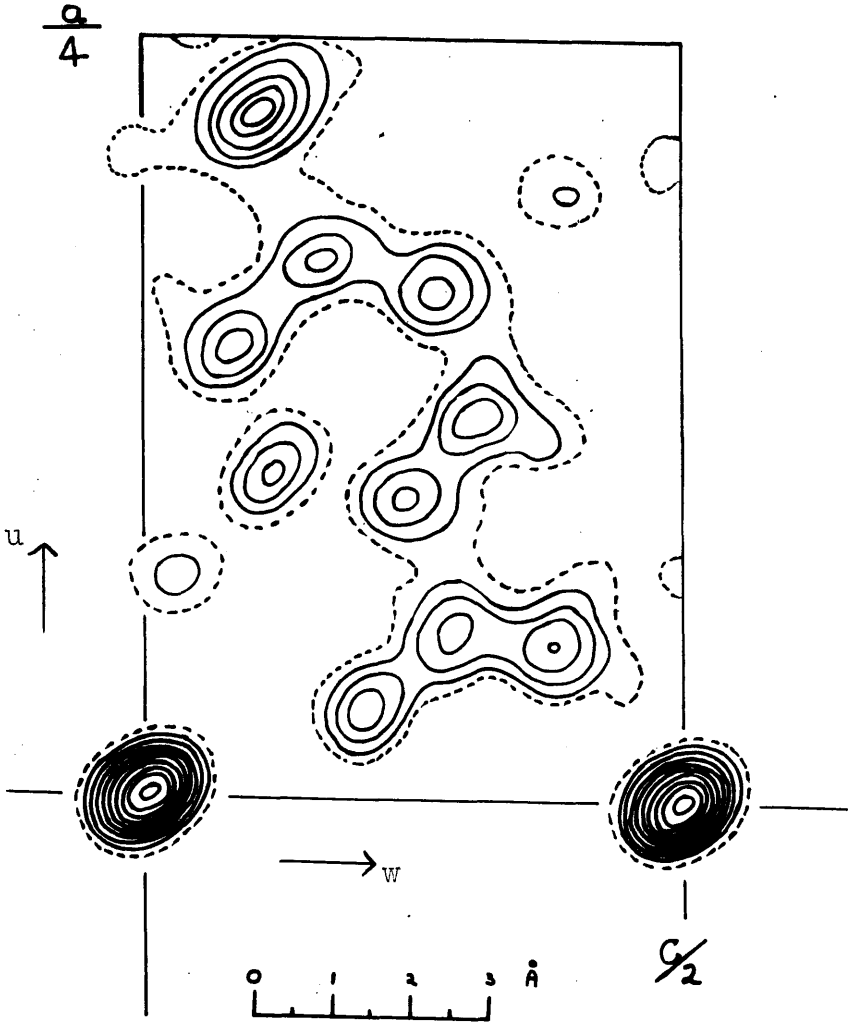


Fig.XIV. Rubidium Hydrogen Di-p-chlorobenzoate: Patterson (010) projection, P(uw). Contours are at equal but arbitrary intervals with zero contour broken.

TABLE 31.

Rubidium Hydrogen Di-p-chlorobenzoate:

Atomic Coordinates from Patterson Projection, P(uw).

Coordinates x and z expressed as fractions of the axial lengths. Origin at rubidium ion.

Atom	x	z
Rb	0.000	0.000
O(1)	0.032	0.208
O(2)	0.050	0.383
C(1)	0.054	0.292
C(2)	0.100	0.250
C(3)	0.125	0.317
C(4)	0.167	0.275
C(5)	0.175	0.167
C(6)	0.150	0.083
C(7)	0.108	0.117
Cl	0.225	0.117

TABLE 22.

Rubidium Hydrogen Di-p-chlorobenzoate:

Final Atomic Coordinates from (010) Projection.

Coordinates x and z are referred to the monoclinic axes and are expressed as fractions of the axial lengths.

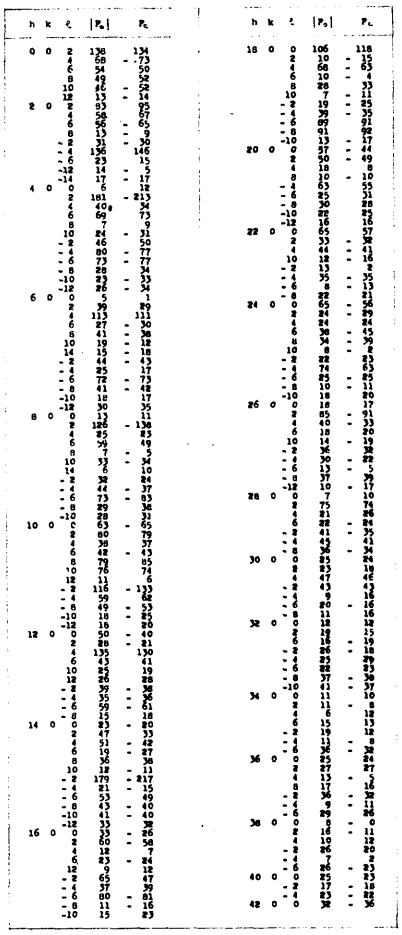
Origin at centre of symmetry on c glide plane.

B is averaged isotropic temperature factor.

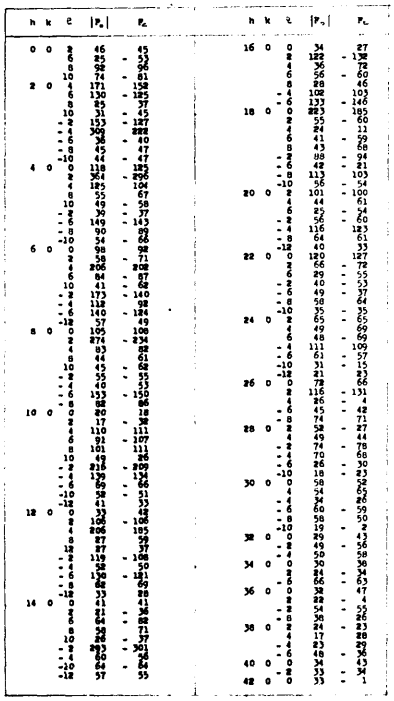
Atom	x	z	B
Rb	0.000	0.2500	3.0
O(1)	0.0328	-0.0452	3.5
O(2)	0.0520	0.1407	3.9
C(1)	0.0541	0.0413	3.4
C(2)	0.0976	-0.0029	4.0
C(3)	0.1268	0.0723	3.8
C(4)	0.1648	0.0351	3.3
C(5)	0.1784	-0.0764	3.3
C(6)	0.1513	-0.1569	4.0
C(7)	0.1079	-0.1179	2.9
Cl	0.2267	-0.1328	4.1

TABLE 23.

(b)



(a)



(a) Rubidium Hydrogen Di-p-chlorobenzoate: Observed structure amplitudes and calculated structure factors, h0ℓ data.

(b) Ammonium Hydrogen Di-p-chlorobenzoate: Observed structure amplitudes and calculated structure factors, h0ℓ data.

AMMONIUM HYDROGEN DI-p-CHLOROBENZOATE.

2.4.8. Experimental.

Ammonium hydrogen di-p-chlorobenzoate was prepared from ammonium hydroxide and p-chlorobenzoic acid in alcohol by mixing stoichiometric quantities; suitable crystals for the X-ray investigation were obtained by recrystallisation from 95% alcohol. The crystals were similar in shape to those of the potassium and rubidium salts. Rotation, oscillation and Weissenberg photographs about the b- and c- axes established the cell dimensions and the halvings.

The hOℓ data were measured visually using the multiple film technique (Robertson, 1943) from Weissenberg photographs taken with Cu Kα radiation. They were corrected for Lorentz and polarisation factors but absorption corrections were not applied. The structure amplitudes obtained were put on an absolute scale by comparison with calculated structure factors; some 191 reflexions were observed.

2.4.9. Crystal Data.

The crystal data for ammonium hydrogen di-p-chlorobenzoate are as follows:

$NH_4H(ClC_7O_2H_4)_2$ M = 330.17

Monoclinic a = 32.8 ± 0.2 Å.

b = 3.88 ± 0.02 Å.

c = 11.44 ± 0.04 Å.

β = 93.0° ± 1°.

Volume of Unit Cell = 1454 Å^3.

$\rho_{obs.}$ = 1.49; calculated on the basis of four molecules in the unit cell, ρ = 1.508.

F(000) = 680.

Absorption Coefficient for X-rays (λ = 1.54 Å) = 42.0 cm^{-1}

Absent Spectra : (hkℓ) h + k = 2n + 1

(h0ℓ) ℓ = 2n + 1

(0k0) k = 2n + 1

Space Group: C^2/c — C^6_{2h} or Cc — C^4_s.

2.4.10. Refinement of the (010) Projection.

Structure factors for the h0ℓ reflexions were calculated using a structure obtained in course of the refinement of the corresponding projection of the potassium salt.

A temperature factor of B = 3 Å^2 was assumed for all the atoms. The scattering factor curves calculated by

Berghuis et al.(1955) for carbon, oxygen and chlorine were used; for the ammonium cation, the scattering curve devised in the refinement of ammonium hydrogen dicinnamate was taken. The R factor was 32.6% which is higher than expected for a supposedly isomorphous structure. A Fourier summation using the observed structure amplitudes and the calculated phases was computed; the resulting map gave an image of the structure without any spurious detail. New atomic coordinates were calculated from the electron-density peak heights in the neighbourhood of each atom and were used in a second structure-factor calculation; the value of R dropped to 17.1%.

Further refinement was by two-dimensional least-squares methods and after four cycles the value of R was 12.2%.

The final atomic coordinates for the (010) projection are shown in Table 24; the table also includes the final averaged isotropic temperature factors. Table 23(b) gives the observed structure amplitudes and the final structure factors on full-scale for the 191 reflexions.

TABLE 24.

Ammonium Hydrogen Di-p-chlorobenzoate:

Final Atomic Coordinates from (010) Projection.

Symbols as in Table 22.

Atom	x	z	B
NH_4	0.0000	0.2500	3.0
O(1)	0.0326	-0.0431	2.7
O(2)	0.0539	0.1384	3.0
C(1)	0.0623	0.0319	3.0
C(2)	0.1037	-0.0092	2.3
C(3)	0.1319	0.0678	3.3
C(4)	0.1707	0.0276	2.8
C(5)	0.1792	-0.0856	3.7
C(6)	0.1519	-0.1597	3.0
C(7)	0.1114	-0.1245	2.7
Cl	0.2261	-0.1401	3.9

POTASSIUM HYDROGEN DI-p-CHLOROBENZOATE.

2.4.11. Experimental.

Potassium hydrogen di-p-chlorobenzoate was prepared by half-neutralising a solution of the acid in alcohol with potassium hydroxide in water. The acid salt crystallised from the mother liquors and the crystals used in this analysis were obtained by recrystallisation from aqueous ethanol.

The cell parameters and halvings were obtained from rotation, oscillation and Weissenberg photographs about the b- and c- axes. The rotation and Weissenberg photographs used to give the cell dimensions were carefully calibrated with powder lines of Cu ($a = 3.6146$ Å) so that the cell dimensions obtained would be free of systematic camera and film shrinkage errors. The density was measured by flotation in a mixture of carbon tetrachloride and bromoform.

The intensity data were measured visually from Weissenberg photographs recording the $h0\ell$, $h1\ell$, $h2\ell$ and $hk0$ nets using the multiple-film technique (Robertson, 1943). The Lorentz and polarization corrections were applied to give the observed structure amplitudes on a relative scale. The data were scaled in the course of the refinement by equating the sum of the observed

structure amplitudes to the sum of the corresponding structure factors for each net. At a later stage in the analysis, absorption corrections were applied to the data from the h0ℓ, h1ℓ and h2ℓ nets. The dimensions of the crystal used were 0.179 mm. x 0.250 mm. and the correction appropriate to a cylindrical crystal of radius 0.1 mm. was applied (International Tables, Vol.II, page 291). The total number of reflexions observed is 790 comprising 195 from the h0ℓ zone, 321 from the h1ℓ net and 274 from the h2ℓ net. Cu Kα radiation was used throughout.

2.4.12. Crystal Data.

The crystal data for potassium hydrogen di-p-chlorobenzoate are shown below:-

$KH(ClC_7O_2H_4)_2$ M = 351.23

Monoclinic a = 33.14 ± 0.08 Å.

b = 3.846 ± 0.02 Å.

c = 11.17 ± 0.04 Å.

$\beta = 90.4^\circ \pm 0.5^\circ$

Volume of the unit cell = 1424 Å^3.

$\rho_{obs.}$ = 1.62; calculated on the basis of four molecules in the unit cell, ρ = 1.638.

F(000) = 712.

Linear absorption coefficient for X-rays ($\lambda = 1.542$ Å), $\mu = 68.4$ cm.$^{-1}$

Absent Spectra: $(hk\ell)$ $h + k = 2n + 1$

$(h0\ell)$ $\ell = 2n + 1$

$(0k0)$ $k = 2n + 1$

Space Group : C^2/c — C_{2h}^6 or Cc — C_s^4 .

2.4.13. Space Group.

The space group is not established uniquely by the absences but, as discussed earlier, the choice of the centrosymmetric space group was made and appears to have been justified by the successful outcome of the analysis based on this assumption.

2.4.14. The (010) Projection.

The final structure obtained from the analysis of the b- axis projection of the rubidium salt was used as the starting structure for this compound. Structure factors were calculated using the following scattering factor curves; Freeman's curve for carbon atom, the curve derived from Freeman's result for an oxygen carrying a half-negative charge, Tomiie and Stam's (1958) curve for chlorine and the values given by Berghuis et al.(1955)

TABLE 25.

Potassium Hydrogen Di-p-chlorobenzoate:

Final Atomic Coordinates from (010) Projection.

Symbols as in Table 22.

Atom	x	z	B
K	0.0000	0.2500	3.0
O(1)	0.0332	-0.0434	3.0
O(2)	0.0495	0.1435	2.8
C(1)	0.0576	0.0394	3.5
C(2)	0.1000	-0.0086	3.0
C(3)	0.1285	0.0708	3.3
C(4)	0.1684	0.0374	2.5
C(5)	0.1786	-0.0834	3.2
C(6)	0.1509	-0.1595	2.8
C(7)	0.1116	-0.1197	3.0
Cl	0.2258	-0.1351	3.2

for the potassium ion. As the potassium ion is sited on a twofold position, a half-scale scattering factor curve was used. Two equivalent positions were used in the structure-factor calculation and the resulting structure factors are on quarter-scale. The value of the disagreement index, R, was 17.5% which shows that the use of the structure of the rubidium salt as a model for the potassium salt is justified. Further refinement was by two-dimensional least-squares methods and the value of R fell to 11.9%. The final structure obtained is shown in Table 25; the coordinates are referred to the origin shown in International Tables for this space group.

2.4.15. Determination of the y-coordinates.

As the b- axis is very short (3.85 Å), the determination of the y-coordinates should not be too difficult. The symmetry of the b- axis projection of the space group C^2/c is p2. In projection the carboxyl group of one p-chlorobenzoate residue is related to another by a centre of symmetry which is the projection of either a centre of symmetry, a screw axis or a twofold axis. The distinction between these can be established by considering the distance in projection between the nearer oxygen atoms

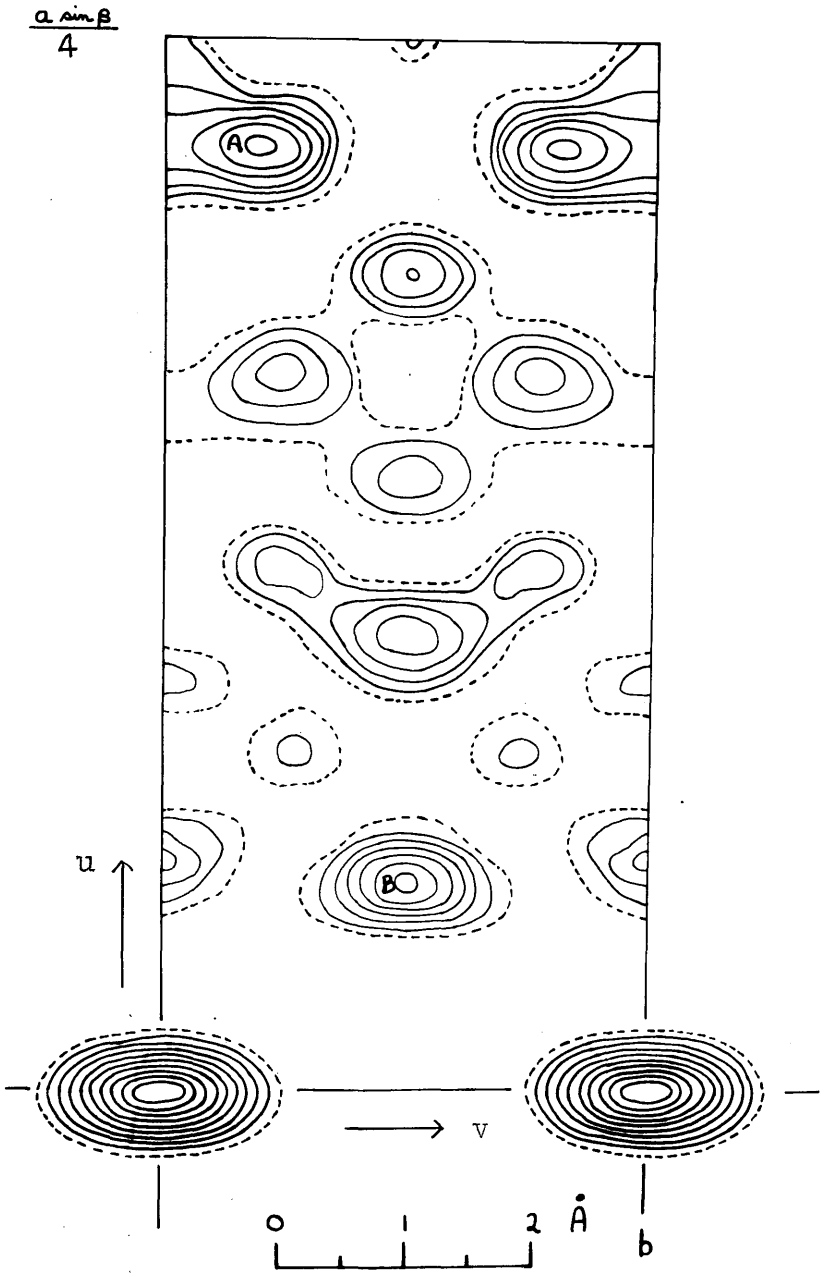


Fig. XV. Potassium Hydrogen Di-p-chlorobenzoate: Patterson (001) projection, P(uv). Contours are at equal but arbitrary intervals with zero contour broken. The K-Cl and Cl-Cl are marked A and B respectively.

of the related p-chlorobenzoate groups. From previous work on acid salts, these oxygen atoms are probably joined by a hydrogen bond of length about 2.50 Å. The distance in projection is 2.41 Å and this suggests that the two oxygen atoms are at different heights and that the difference in height is .45 Å. The twofold axis and the screw axis are immediately ruled out and the oxygen atoms must be related by a centre of symmetry which is taken as the origin. This establishes the position of origin in relation to the p-chlorobenzoate groups and the potassium ion.

The angle of tilt of the benzene ring is easily found from the two-dimensional study. An attempt was made to use this information with the position of the oxygen atom involved in the hydrogen bond to give the y-coordinates. This failed as the carboxyl group and the benzene ring were not planar as expected.

The hkO data were used in a Patterson synthesis P(uvO); this is illustrated in Fig.XV. The interpretation of this was hampered by the presence of two equally-heavy atoms in the asymmetric unit, one of which is situated on a twofold axis. The K - Cl and Cl - Cl vectors are easily identified and are marked by the symbols A and B on the

diagram. This established the height of the chlorine atom with respect to the potassium atom. The K - K vectors occur in the origin peak and account for its elongation in the v- direction. From this information a large number of possible potassium and chlorine positions were obtained and, although the correct solution was included in the possibilities, it was not recognised at this stage.

The problem was finally solved by comparing the data for this compound with the results of the studies of potassium hydrogen di-p-hydroxybenzoate (Skinner and Speakman, 1951) and potassium hydrogen dibenzoate (Skinner, Stewart and Speakman, 1954). The cell dimensions and space group for all three compounds are shown in Table 26.

Weighted reciprocal lattices of the (001) projection were drawn for the three compounds. These lattices are very similar and could be compared directly to give phases for potassium hydrogen di-p-chlorobenzoate from the phases of the other two. A Fourier synthesis was computed with these phases and the observed structure amplitudes. The electron-density map produced gave an image of the molecule and, from it, atomic positions for all the atoms were obtained. These atomic positions were consistent with the a- axis coordinates already obtained from the h0ℓ

TABLE 26.

Cell Dimensions and Space Groups

of the Potassium Acid Salts of some Carboxylic Acids.

Acid	a	b	c	β	Space Group
Benzoic*	29.53	3.88	11.20	95.8°	C2/c
p-OH Benzoic*	16.40	3.82	11.30	92.5°	P2/c
p-Cl Benzoic	33.14	3.85	11.17	90.4°	C2/c

* For references, see Table 38.

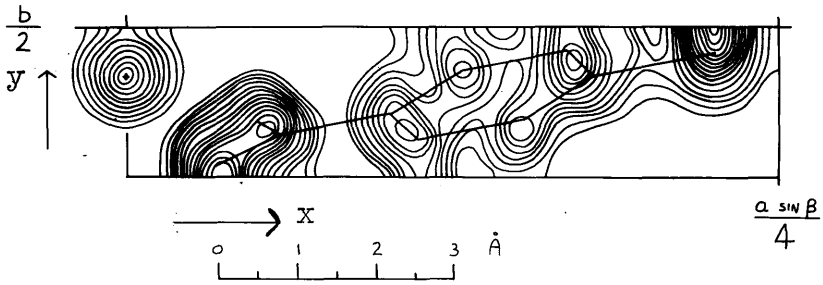


Fig. XVI. Potassium Hydrogen Di-p-chlorobenzoate: Electron-density projected along c-axis. Contour-line interval : for lighter atoms, 1 electron per square Å, starting from 2; for potassium ion, 2.5 electrons per square Å, starting from 2.5; for chlorine atom, 2, 3, 4, 7.5 and 2.5 electrons per square Å thereafter.

TABLE 27.

Potassium Hydrogen Di-p-chlorobenzoate:

Final Atomic Coordinates from (001) Projection.

Coordinates x and y are referred to the monoclinic axes and are expressed as fractions of the axial lengths.

Atom	x	y
K	0.0000	0.3400
O(1)	0.0332	0.0500
O(2)	0.0495	0.1850
C(1)	0.0576	0.1450
C(2)	0.1000	0.2100
C(3)	0.1285	0.3600
C(4)	0.1684	0.4200
C(5)	0.1786	0.3500
C(6)	0.1509	0.1900
C(7)	0.1116	0.1250
Cl	0.2258	0.4200

projection and produced the interatomic vectors in the Patterson map. Structure factors were calculated using the scattering factor curves described previously and a temperature factor of B = 3 $\AA^2$ for all atoms; the value of R was 35%. Four cycles of refinement by Fourier-syntheses methods reduced the value of R to 16.7%. During the refinement, the a- axis coordinates were held constant at the values obtained for the (010) projection.

The final Fourier synthesis for this projection is shown in Fig.XVI; Table 27 gives the atomic coordinates obtained from the Fourier map.

2.4.16. Partial Three-dimensional Refinement.

The structures obtained from the two-dimensional studies were combined to give the atomic coordinates in three-dimensions. Initially, it was noticed that structure factors calculated for the hlℓ reflexions were in poor agreement with the observed structure amplitudes when ℓ was odd. This was remedied by changing the potassium ion coordinate from the obvious combination (0.000, 0.340, 0.250) to the other possible combination (0.000, 0.660, 0.250). The values of the discrepancy for the two zones, hlℓ and h2ℓ, were 17.1% and 20.8%.

The course of the least-squares refinement is shown in Table 28. The data used were the reflexions from the h0ℓ, h1ℓ and h2ℓ nets and the value of R quoted in this table is the overall value. Details of the least-squares program are found elsewhere. The $\sqrt{w_2}$ weighting system was used with a value of 7.68 for F^*. The initial isotropic temperature factor was the average of the anisotropic values obtained at the end of the (010) two-dimensional refinement.

All the atoms except the potassium ion were included in the least-squares refinement. At the beginning of each phase of refinement, the y- coordinate and the isotropic temperature factor of the potassium ion were adjusted from information contained in F_o, F_c and $(F_o - F_c)$ maps computed in the vicinity of the potassium ion using the phases at that stage. In the first two phases of refinement, the anisotropic temperature factors were analysed at the end of each cycle and averaged to give isotropic values to be used in the next cycle.

Positions were assigned to the hydrogen atoms of the benzene ring by assuming that the distance across a benzene ring is 2.78 Å and that the carbon-hydrogen bond length is 1.07 Å. The hydrogen atoms were included in the structure-factor calculation with a temperature factor $B = 4$ Å^2 for

TABLE 28.

Potassium Hydrogen Di-p-chlorobenzoate:

Progress of Refinement.

Phase	Cycle	R	$\Sigma w\Delta^2$	Notes.
A	1	18.3%	219	
	2	17.6	204	
	3	16.7	188	
	4	16.4	179	
B	1	15.9	170	Hydrogen Atom in S.F.
	2	15.7	*	
C	1	15.1	155	Data corrected for absorption.
	2	14.3	131	
	3	12.8	116	
D	1	12.4	27	Half-Scale form cards.
	2	12.1	21	
	3	11.9	21	
	4	11.8	*	

* Not Calculated.

the benzene-ring hydrogen atoms and $B = 5$ $\AA^2$ for the acidic hydrogen atom; the scattering-factor curve devised by McWeeny (1951) was used. The positions of the hydrogen atoms were not refined but, prior to the final phase, their coordinates were recalculated using the carbon atom coordinates at the end of the penultimate phase.

Absorption corrections were applied to the data before the start of phase C.

The structure factors of the reflexions in the three nets which were not observable were calculated and those reflexions, whose structure factors suggested that they should have been observable, were included in the final two phases of refinement with an intensity value equal to half the minimum observable. These intensity values were corrected for absorption, Lorentz and polarisation factors and scaled in the same way as the observed data. This means that the final structure is weighted to minimise the structure factors of these terms.

The L.S. program would not solve the normal equations for the chlorine atom. The term $\sum(\partial\Delta/\partial b_{11} . \partial\Delta/\partial b_{11})$ was too large and, as a result, had overflowed. As b_{11} has dimensions f^2h^4, where f is the scattering factor value and h is the Miller index and b_{11} refers to an axis

of length, 33.1 Å, it is not surprising that this has happened. To accommodate this term in DEUCE, the structure factors were calculated using half-scale scattering factor curves. This now gives structure factors which are on one-eighth of the absolute scale.

The final calculated structure factors and the observed structure amplitudes on full-scale are shown in Table 29; the unobserved terms in the least-squares refinement are also included.

The final value of R is 11.8%, excluding the unobserved terms; for the individual nets, the values are 12.3% (h0ℓ), 10.9% (h1ℓ) and 13.0% (h2ℓ). Structure factors for the h0ℓ zone were calculated neglecting the contributions of the hydrogen atoms and the value of R increased to 13.1%.

2.4.17. Final Structure, Molecular Dimensions and Estimates of Accuracy.

The final atomic coordinates are shown in Table 30. The temperature parameters obtained at the end of the least-squares refinement are listed in Table 31; these are the parameters in the equation,

$$\exp(-B \sin^2\theta/\lambda^2) = 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + b_{12}hk + b_{23}k\ell + b_{31}h\ell)}.$$

TABLE 29.

Potassium Hydrogen Di-p-chlorobenzoate.

h	k	ℓ	$\lvert F_o \rvert$	F_c
0	0	2	86	101
		4	63	- 51
		6	16	3
		8	60	- 48
		10	20	0
0	2	1	44	- 57
		2	14	11
		3	22	21
		4	13	- 18
		5	10	9
		7	32	- 34
		9	26	- 29
		11	11	11
		12	23	- 21
		13	5	0
1	1	1	107	- 110
		2	16	25
		3	21	- 24
		4	13	7
		5	47	46
		6	94	- 86
		7	56	- 54
		9	12	12
		10	11	- 9
		11	168	- 183
		12	103	105
		13	90	- 82
		14	48	- 50
		15	14	11
		16	12	- 13
		17	11	8
		18	13	- 15
		19	26	26
		20	22	- 19
2	0	2	60	50
		4	103	98
		6	65	- 75
		8	13	- 16
		10	14	14
		12	58	- 56
		14	167	172
		16	12	6
		18	24	- 24
		20	9	17
2	2	1	44	- 46
		2	20	24
		3	39	36
		4	67	70
		5	20	28
		6	36	- 36
		7	17	25
		8	25	- 23
		9	31	28
		10	21	- 21
		11	11	12
		12	13	- 14
		13	7	9
		14	41	- 39
		15	23	24
		16	33	- 32
		17	34	- 30
		18	14	18
3	1	0	94	96
		1	113	- 111
		2	207	218
		3	97	- 92
		4	20	22
		5	61	63
		6	17	- 17
		7	24	23
		8	20	- 22
		9	55	54
		10	35	- 39
		11	32	34
		12	96	- 96
		13	43	50
		14	33	- 32
		15	20	21
		16	10	- 9
		17	7	7
4	0	0	46	- 37
		2	225	- 223
		4	61	58
		6	52	40
		8	24	29
		10	38	- 40
		12	23	25
		14	42	- 42
		16	91	- 92
		18	37	40
		20	36	- 40
		22	23	29
4	2	1	197	- 186
		2	53	50
		3	16	- 18
		4	15	15
		5	33	33
		6	10	- 18
		7	10	16
		8	31	- 31
		9	25	26
		10	15	- 11
		11	9	1
		12	8	- 7
		13	41	- 37
		14	40	40
		15	33	- 38
		16	4	8
5	1	0	120	- 128
		1	62	61
		2	71	- 66
		3	28	10
		4	52	42
		5	35	31
		6	39	44
		7	20	- 19
		8	11	11
		9	29	- 28
		10	11	11
		11	90	- 85
		12	129	133
		13	28	24
		14	45	- 36
		15	40	39
		16	23	- 23
		17	16	5
		18	27	30
		19	44	43
6	0	0	45	45

h	k	ℓ	$\lvert F_o \rvert$	F_c
6	0	4	140	137
		6	55	- 51
		8	24	24
		10	24	- 31
		12	9	10
		14	12	- 18
		16	12	16
		18	4	- 4
		20	4	4
6	2	0	20	- 15
		2	88	83
		4	26	- 30
		5	4	0
		6	44	- 48
		7	59	66
		8	19	- 19
		9	31	25
		10	20	19
		11	10	- 12
		12	11	9
		13	9	- 16
		14	81	67
		15	30	- 30
		16	27	23
		17	14	- 12
		18	38	36
		19	10	- 7
		20	9	0
7	1	0	11	5
		1	38	36
		2	5	4
		3	33	- 32
		4	72	72
		5	23	- 23
		6	47	53
		7	37	- 36
		8	39	44
		9	10	16
		10	12	- 12
		11	80	75
		12	13	- 12
		13	17	18
		14	22	- 17
		15	23	24
		16	10	- 10
		17	11	14
		18	6	- 6
		19	38	34
		20	9	- 8
8	0	0	57	50
		2	107	- 176
		4	37	38
		6	36	24
		8	21	27
		10	35	- 37
		12	14	18
		14	6	- 6
		16	102	- 107
		18	64	66
		20	25	38
		22	34	- 16
8	2	0	8	- 5
		1	7	17
		2	22	- 25
		3	30	30
		4	128	- 120
		5	16	19
		6	31	- 30
		7	15	19
		8	14	- 12
		9	32	27
		10	14	- 14
		11	12	11
9	1	0	108	- 107
		1	62	58
		2	73	74
		3	35	33
		4	72	65
		5	22	30
		6	19	19
		7	14	- 20
		8	50	60
		9	10	23
		10	15	12
		11	160	- 100
		12	30	31
		13	45	41
		14	17	16
		15	6	9
		16	15	10
		17	39	- 36
		18	45	42
		19	43	45
		20	9	5
10	0	0	39	- 35
		2	48	37
		4	64	73
		6	67	- 65
		8	44	37
		10	66	58
		12	15	21
		14	137	- 145
		16	75	72
		18	30	- 27
		20	17	16
		22	7	- 28
10	2	0	9	8
		1	11	- 16
		2	39	37
		3	7	0
		4	26	- 20
		5	27	40
		6	22	27
		7	11	- 5
		8	31	30
		9	73	- 80

h	k	ℓ	$\lvert F_o \rvert$	F_c
10	2	3	79	- 74
		4	62	55
		5	24	- 24
		6	23	20
		7	21	- 15
		8	16	20
		9	35	- 31
		10	15	14
11	1	0	5	- 14
		1	45	50
		2	16	23
		3	38	- 38
		4	50	52
		5	25	32
		6	16	- 18
		7	14	8
		8	13	- 10
		9	15	14
		10	16	- 15
		11	16	13
		12	114	- 110
		13	48	40
		14	23	21
		15	25	- 25
		16	30	22
		17	8	- 19
		18	16	16
		19	10	- 9
		20	8	0
12	0	0	27	- 21
		2	65	67
		4	154	- 156
		6	33	27
		8	22	- 28
		10	40	44
		12	18	- 13
		14	7	8
		16	120	- 90
		18	31	28
		20	12	- 8
12	2	0	24	16
		1	40	- 40
		2	32	33
		3	26	- 30
		4	7	8
		5	22	27
		6	26	- 24
		7	11	13
		8	14	- 18
		9	6	0
13	1	0	114	- 121
		1	73	73
		2	37	- 40
		3	61	61
		4	22	- 19
		5	52	52
		6	14	- 14
		7	30	28
		8	15	- 13
		9	19	20
		10	41	- 39
		11	36	33
		12	16	- 12
		13	76	71
		14	39	- 36
		15	25	16
		16	21	- 19
		17	38	25
		18	83	- 76
		19	54	44
		20	8	- 7
14	0	0	17	12
		2	30	- 33
		4	14	11
		6	41	- 45
		8	42	47
		10	16	- 20
		12	24	16
		14	6	- 13
		16	24	29
		18	11	- 9
		20	45	36
14	2	1	10	8
		2	15	- 23
		3	28	25
		4	25	- 31
		5	33	36
		6	23	- 24
		7	24	24
		8	14	- 11
		9	18	18
		10	5	- 13
		11	14	6
		12	18	- 14
		13	21	24
		14	32	- 28
		15	20	18
		16	17	- 17
		17	34	30
		18	15	- 13
		19	10	10
		20	3	- 10
15	1	1	25	31
		2	20	- 13
		3	58	56
		4	40	- 44
		5	46	50
		6	20	- 24
		7	17	7
		8	10	- 5
		9	37	36
		10	18	- 18
		11	78	75
		12	60	- 55
		13	41	35
		14	15	- 8
		15	9	11
		16	19	15
		17	18	- 18
		18	17	16
		19	26	- 26
16	0	0	28	19
		2	12	- 11
		4	17	16
		6	39	- 41
		8	12	16
		10	8	- 2

h	k	ℓ	$\lvert F_o \rvert$	F_c
16	0	4	67	66
		6	117	- 105
		8	27	31
		12	17	16
16	2	0	41	- 41
		1	22	29
		2	25	- 28
		3	27	28
		4	23	- 23
		5	38	40
		6	28	27
		7	10	- 5
		8	12	10
		9	13	- 14
		10	30	25
		11	17	- 16
		12	51	49
		13	9	3
		14	26	- 23
		15	27	24
		16	10	- 3
		17	73	79
		18	66	- 58
		19	35	36
		20	41	- 42
		21	27	27
		22	16	- 21
		23	26	29
		24	10	- 19
		25	8	8
17	1	0	191	145
		1	7	- 17
		2	47	34
		3	56	- 35
		4	37	41
		5	50	- 49
		6	34	36
		7	63	- 60
		8	93	83
		9	41	- 38
		10	29	33
		11	18	- 16
		12	18	23
		13	93	- 98
		14	17	19
		15	9	- 17
		16	20	20
		17	25	- 20
		18	26	20
		19	9	- 7
		20	15	15
18	2	3	33	- 33
		4	34	33
		5	18	- 19
		6	10	16
		7	18	- 23
		8	15	16
		9	25	- 20
		10	20	20
		11	35	- 37
		12	21	19
		13	9	7
		14	27	- 23
		15	28	19
		16	9	- 7
		17	5	1
		18	48	- 47
		19	24	26
		20	13	- 15
19	1	0	15	9
		1	27	- 25
		2	32	32
		3	24	- 24
		4	9	7
		5	33	- 33
		6	19	24
		7	13	- 13
		8	15	15
		9	20	- 20
		10	18	18
		11	16	- 15
		12	6	6
		13	18	- 18
		14	20	20
		15	9	- 9
		16	14	14
		17	17	- 15
		18	34	32
		19	10	- 10
		20	5	0
20	0	0	18	- 18
		2	46	46
		4	26	- 30
		6	20	25
		8	12	- 6
		10	37	36
		12	19	- 15
		14	43	48
		16	45	- 43
		18	29	27
		20	56	- 56
20	2	0	28	31
		1	28	- 33
		2	25	30
		3	26	- 25
		4	8	6
		5	23	- 24
		6	24	24
		7	14	- 11
		8	18	18
		9	13	- 15
		10	5	0
		11	14	- 14
		12	20	18
		13	21	- 18
		14	20	20
		15	11	- 8
		16	4	0
22	0	0	81	88
		2	10	- 13
		4	38	27
		6	13	- 22
		8	12	21
		10	5	- 21
		12	7	6
		14	16	- 19
		16	17	17
		18	8	- 16
		20	4	0
22	2	1	10	3
		2	95	- 87
		3	8	10
		4	15	- 17
		5	17	14
		6	12	- 6
		7	26	26
		8	11	- 10
		9	20	17
		10	20	- 20
		11	6	5
		12	34	- 32
		13	9	12
		14	37	- 37
		15	2	2
		16	67	- 69
		17	38	40
		18	16	- 16
		19	30	30
		20	13	- 13
23	1	1	26	23
		2	59	- 53
		3	9	14
		4	9	- 16
		5	21	27
		6	13	- 17
		7	28	28
		8	24	- 25
		9	36	31
		10	3	- 3
		11	38	40
		12	16	- 16
		13	30	30
		14	13	- 13
		15	6	8
		16	18	- 21
		17	8	8
		18	36	- 36
		19	6	6
		20	16	- 15
24	0	0	27	16
		2	38	- 38
		4	36	38
		6	39	- 45
		8	26	18
		10	8	- 14
		12	68	66
		14	33	- 31
		16	11	8
		18	21	17
		20	30	- 29
24	2	1	49	49
		2	25	- 29
		3	25	29
		4	17	- 20
		5	19	22
		6	8	- 7
		7	10	5
		8	11	- 14
		9	11	11
		10	35	- 37
		11	21	19
		12	25	- 26
		13	7	8
		14	28	- 19
		15	9	7
		16	20	- 20
		17	23	23
		18	6	- 6
		19	20	20
		20	9	- 8
25	1	0	15	12
		1	20	- 20
		2	14	20
		3	31	- 36
		4	30	36
		5	16	- 17
		6	9	9
		7	10	- 14
		8	9	11
		9	11	- 11
		10	26	25
		11	25	- 28
		12	7	19
		13	28	- 7
		14	9	1
		15	10	- 7
		16	5	1
		17	48	- 47
		18	22	26
		19	6	- 6
		20	20	20
26	0	0	47	47
		2	99	- 106
		4	38	28
		6	13	21
		8	30	26
		10	17	- 17
		12	23	23
		14	61	- 58
		16	15	11
		18	20	23
		20	9	- 12
26	2	0	31	36
		1	9	- 9
		2	8	7
		3	31	36
		4	11	- 9
		5	11	12
		6	17	- 22
		7	24	23
		8	9	- 5
		9	11	9
		10	17	- 15
		11	30	34
		12	15	- 13
		13	10	10
		14	3	- 10
		15	16	16
		16	7	- 7
		17	15	14
		18	21	- 16
		19	22	24
		20	34	- 34
28	0	2	39	34
		4	25	- 33
		6	25	26
		8	11	- 16
		10	6	2
		12	49	- 51
		14	43	43
		16	18	- 18
		18	20	20
		20	17	- 20
28	2	1	20	20
		2	17	- 20
		3	7	7
		4	5	- 5
		5	30	33
		6	4	- 2
		7	26	26
		8	19	- 17
		9	7	9
		10	14	- 12
		11	13	13
		12	16	- 15
		13	20	19
		14	8	- 15
29	1	0	20	18
29	1	1	15	17
		2	15	24
		3	29	- 29
		4	23	27
		5	23	- 27
		6	11	15
		7	24	- 27
		8	19	19
		9	10	- 17
		10	11	7
		11	7	- 4
		12	16	14
		13	24	- 22
30	0	0	25	30
		2	20	21
		4	13	- 9
		6	34	33
		8	3	- 3
30	2	1	17	22
		2	17	23
		3	20	- 23
		4	21	28
		5	11	- 5
		6	8	14
		7	24	- 22
		8	13	9
		9	7	- 9
		10	34	33
		11	3	- 3
31	1	0	31	35
		1	7	- 7
		2	23	23
		3	20	- 23
		4	20	24
		5	11	- 8
		6	8	14
		7	15	- 19
		8	16	16
		9	22	- 22
		10	16	15
		11	4	- 4
32	0	0	20	24
		2	13	8
		4	18	- 21
		6	25	25
		8	33	30
		10	26	- 24
		12	17	20
32	2	1	14	8
		2	16	18
		3	8	3
		4	13	- 16
		5	7	7
		6	24	25
		7	14	- 17
		8	30	35
		9	7	5
		10	15	- 15
		11	7	10
33	1	0	27	25
		1	10	- 13
		2	9	13
		3	14	- 17
		4	20	23
		5	14	- 17
		6	35	33
		7	23	- 21
		8	4	0
34	0	0	15	- 21
		2	12	20
		4	10	7
		6	47	- 53
		8	12	15
34	2	1	9	15
		2	12	12
		3	20	- 24
		4	12	14
		5	19	- 21
		6	15	15
35	1	0	15	18
		1	14	- 18
		2	18	24
		3	10	- 6
		4	14	13
		5	17	- 19
		6	15	15
		7	34	26
36	0	0	20	- 24
		2	22	18
		4	16	- 16
		6	43	48
		8	16	17
		10	19	- 19
		12	23	23
37	1	0	10	- 9
		1	9	15
		2	11	11
		3	6	- 11
		4	14	15
		5	18	- 18
		6	31	32
		7	14	12
		8	8	- 8
38	0	2	13	16
		4	5	- 11
		6	21	22
		8	36	- 36
38	2	0	21	19
		2	13	- 13
39	1	0	10	18
		1	10	- 13
		2	16	20
		3	7	- 11
		4	16	17
		5	7	- 7
		6	7	5
40	0	0	30	33
		2	4	- 2
		4	20	26
		6	19	- 17
41	1	1	6	9
		2	14	- 12
		3	13	18
		4	4	- 5
		5	14	15
42	0	0	20	- 19
		2	8	15

h	k	ℓ	$\lvert F_o \rvert$	F_c
1	1	8	6	- 15
1	1	10	7	12
2	0	12	7	10
2	0	14	7	9
3	1	11	6	- 8
4	0	12	7	8
6	0	8	6	- 10
7	1	10	6	11

h	k	ℓ	$\lvert F_o \rvert$	F_c
8	2	7	5	- 3
8	2	9	5	6
10	2	7	5	- 7
11	1	10	6	8
12	0	10	8	- 7
12	2	8	5	10
12	2	8	6	- 12
13	1	8	6	12

h	k	ℓ	$\lvert F_o \rvert$	F_c
13	1	9	6	- 12
14	0	12	6	8
15	1	9	6	- 13
15	1	11	5	6
16	0	12	5	- 15
16	2	7	5	4
16	2	10	4	- 4

h	k	ℓ	$\lvert F_o \rvert$	F_c
16	2	11	3	10
17	1	9	5	8
18	0	12	5	- 2
18	2	- 5	5	8
21	1	10	5	- 18
22	0	- 6	8	8
24	2	- 5	5	7

h	k	ℓ	$\lvert F_o \rvert$	F_c
24	2	7	2	12
25	1	6	6	13
26	0	6	8	8
26	0	8	7	14
27	1	6	6	10
28	0	0	7	18

h	k	ℓ	$\lvert F_o \rvert$	F_c
28	0	- 6	8	- 5
29	1	6	6	11
30	2	0	5	10
32	0	4	4	4
32	2	4	4	- 5
33	1	1	4	7
34	0	0	7	13

Observed structure amplitudes and final calculated structure factors. The lower table gives the unobserved reflexions included in the least-squares refinement. In this case, the value of $|F_o|$ is the minimum locally observable.

TABLE 30.

Potassium Hydrogen Di-p-chlorobenzoate:

Final Atomic and Calculated Hydrogen Coordinates.

Coordinates x, y and z are expressed as fractions of the axial lengths and are referred to the monoclinic crystal axes. Coordinates X, Y and Z' are in Angstroms and are referred to the orthogonal system a, b and c*. Origin at centre of symmetry on c glide plane.

Atom	x	y	z	X	Y	Z'
K	0.0000	0.6417	0.2500	-0.020	2.468	2.793
O(1)	0.0335	0.0437	-0.0446	1.112	0.168	-0.498
O(2)	0.0492	0.1851	0.1420	1.619	0.712	1.587
C(1)	0.0593	0.1452	0.0379	1.963	0.558	0.423
C(2)	0.1011	0.2050	-0.0056	3.350	0.788	-0.063
C(3)	0.1288	0.3564	0.0730	4.264	1.371	0.815
C(4)	0.1677	0.4198	0.0335	5.554	1.614	0.374
C(5)	0.1785	0.3302	-0.0808	5.921	1.270	-0.903
C(6)	0.1517	0.1693	-0.1573	5.040	0.651	-1.758
C(7)	0.1125	0.1054	-0.1184	3.737	0.405	-1.323
Cl	0.2262	0.4324	-0.1352	7.506	1.663	-1.511

Calculated Hydrogen Coordinates

H(1)	0.120	0.422	0.160	3.96	1.62	1.78
H(2)	0.189	0.540	0.092	6.24	2.08	1.03
H(3)	0.160	0.111	-0.244	5.32	0.43	-2.73
H(4)	0.091	-0.032	-0.177	3.04	-0.12	-1.98

TABLE 31.

Potassium Hydrogen Di-p-chlorobenzoate:
Anisotropic Thermal Parameters.

($b_{ij} \times 10^5$)

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
K	98	7314	867	-	4	-
O(1)	83	13380	945	-820	175	-401
O(2)	116	8022	1004	- 3	271	- 82
C(1)	107	5480	798	-	148	-328
C(2)	93	6339	727	629	196	38
C(3)	121	7217	686	-1268	117	-196
C(4)	120	5531	795	-	113	96
C(5)	84	4515	1160	1506	124	110
C(6)	101	6197	742	386	154	269
C(7)	99	6729	942	-	124	-144
Cl	91	9335	1335	193	287	-294
All H ($B = 6.0$ Å^2)	197	14629	1734	-	8	-

TABLE 32.

Potassium Hydrogen Di-p-chlorobenzoate:

Bond Lengths (Å).

Atoms	Distance	Atoms	Distance
O(1) - C(1)	1.313 Å	C(5) - C(6)	1.375 Å
O(2) - C(1)	1.223	C(6) - C(7)	1.396
C(1) - C(2)	1.487	C(7) - C(2)	1.373
C(2) - C(3)	1.395	C(5) - Cl	1.742
C(3) - C(4)	1.385	K .... O(2)	2.687
C(4) - C(5)	1.372	O(1)....O(1)'	2.460

TABLE 33.

Potassium Hydrogen Di-p-chlorobenzoate:

Bond Angles.

Atoms	Angle	Atoms	Angle
O(1) - C(1) - O(2)	121.5°	C(5) - C(6) - C(7)	119.0°
O(1) - C(1) - C(2)	114.9	C(6) - C(7) - C(2)	120.0
O(2) - C(1) - C(2)	123.6	C(7) - C(2) - C(1)	121.3
C(1) - C(2) - C(3)	118.1	C(7) - C(2) - C(3)	120.6
C(2) - C(3) - C(4)	118.9	C(4) - C(5) - Cl	120.7
C(3) - C(4) - C(5)	120.1	C(6) - C(5) - Cl	117.9
C(4) - C(5) - C(6)	121.4	C(1) - O(1)...O(1)'	110.1

TABLE 34.

Potassium Hydrogen Di-p-chlorobenzoate:

Intermolecular Distances < 3.846 Å.

Atoms	Distance	Atoms	Distance
$O(2)\ldots O(1)^{I}$	3.65 Å	$C(2)\ldots C(7)^{VI}$	3.71 Å
$O(2)\ldots C(7)^{I}$	3.57	$C(3)\ldots C(1)^{VI}$	3.83
$C(3)\ldots C(6)^{I}$	3.70	$C(3)\ldots C(2)^{VI}$	3.50
$Cl \ldots Cl^{II}$	3.68	$C(3)\ldots C(7)^{VI}$	3.63
$O(1)\ldots O(1)^{III}$	2.46	$C(4)\ldots C(2)^{VI}$	3.77
$O(1)\ldots O(2)^{III}$	3.07	$C(4)\ldots C(5)^{VI}$	3.75
$O(1)\ldots C(1)^{III}$	3.16	$C(4)\ldots C(6)^{VI}$	3.62
$Cl\ldots Cl^{IV}$	3.58	$C(4)\ldots C(7)^{VI}$	3.62
$C(3)\ldots C(6)^{V}$	3.60	$C(5)\ldots C(6)^{VI}$	3.45
$C(4)\ldots C(6)^{V}$	3.84	$Cl\ldots C(6)^{VI}$	3.77
$C(1)\ldots O(1)^{VI}$	3.68		

TABLE 35.

Potassium Hydrogen Di-p-chlorobenzoate:

Potassium ion - Oxygen Distances.

Atoms	Distance.
K ...O(2)	2.687 Å
K ... $O(2)^{VII}$	2.687
K ... $O(2)^{VIII}$	2.916
K ... $O(2)^{VI}$	2.916
K ... $O(1)^{V}$	2.815
K ... $O(1)^{IX}$	2.815

In Tables 34 and 35, the superscripts refer to the following positions:-

I	$x, \bar{y}, \frac{1}{2}+z$	VI	$x, 1+y, z$
II	$\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$	VII	$\bar{x}, y, \frac{1}{2}-z$
III	$\bar{x}, \bar{y}, \bar{z}$	VIII	$\bar{x}, 1+y, \frac{1}{2}-z$
IV	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$	IX	$\bar{x}, 1-y, \bar{z}$
V	$x, 1-y, \frac{1}{2}+z$		

TABLE 36.

Potassium Hydrogen Di-p-chlorobenzoate:

Standard Deviations of the Final

Atomic Coordinates (Å).

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
O(1)	0.0062	0.0099	0.0067
O(2)	0.0066	0.0096	0.0068
C(1)	0.0092	0.0136	0.0090
C(2)	0.0088	0.0135	0.0090
C(3)	0.0097	0.0136	0.0090
C(4)	0.0096	0.0135	0.0095
C(5)	0.0087	0.0135	0.0101
C(6)	0.0092	0.0134	0.0091
C(7)	0.0091	0.0140	0.0095
Cl	0.0024	0.0040	0.0029

TABLE 37.

Potassium Hydrogen Di-p-chlorobenzoate:

Deviations from the Mean Planes.

(a) Plane through C(1), ... , C(7) and Cl.

(b) Plane through C(2), ... , C(7) and Cl.

(c) Plane through C(1), ..., C(6) and C(7).

(d) Plane through C(2), ..., C(6) and C(7) i.e. benzene ring.

(e) Plane through O(1), O(2), C(1) and C(2).

Atom	(a)	(b)	(c)	(d)	(e)
O(1)	(-0.257)				0.000
O(2)	(+0.099)				0.000
C(1)	-0.051		-0.014		-0.001
C(2)	-0.015	-0.044	-0.006	-0.018	0.000
C(3)	+0.023	+0.002	+0.018	+0.011	
C(4)	+0.033	+0.029	+0.002	+0.005	
C(5)	+0.023	+0.027	-0.021	-0.014	
C(6)	+0.036	+0.032	+0.004	+0.007	
C(7)	+0.021	0.000	+0.016	+0.009	
Cl	-0.070	-0.045		(-0.128)	

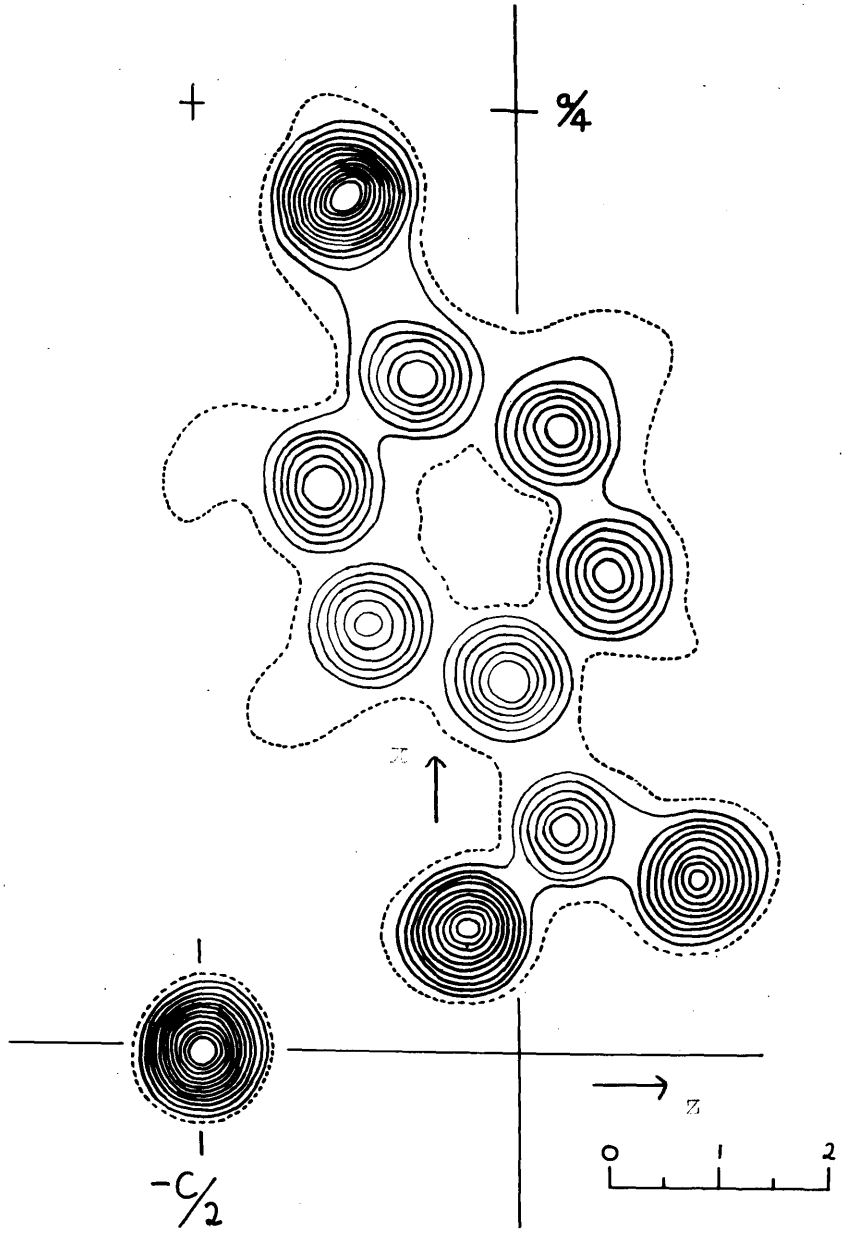


Fig. XVII. Potassium Hydrogen Di-p-chlorobenzoate: Electron-density projected along b-axis. Contour-line interval: for lighter atoms, 1 electron per square Å with 1 drawn as broken line; for chlorine, 1 (broken line), 2, 3, 4, 5 and thereafter at an interval of 2.5 electrons per square Å; for potassium ion, 2 (broken line), 3, 4, 5 and thereafter at an interval of 2.5 electrons per square Å.

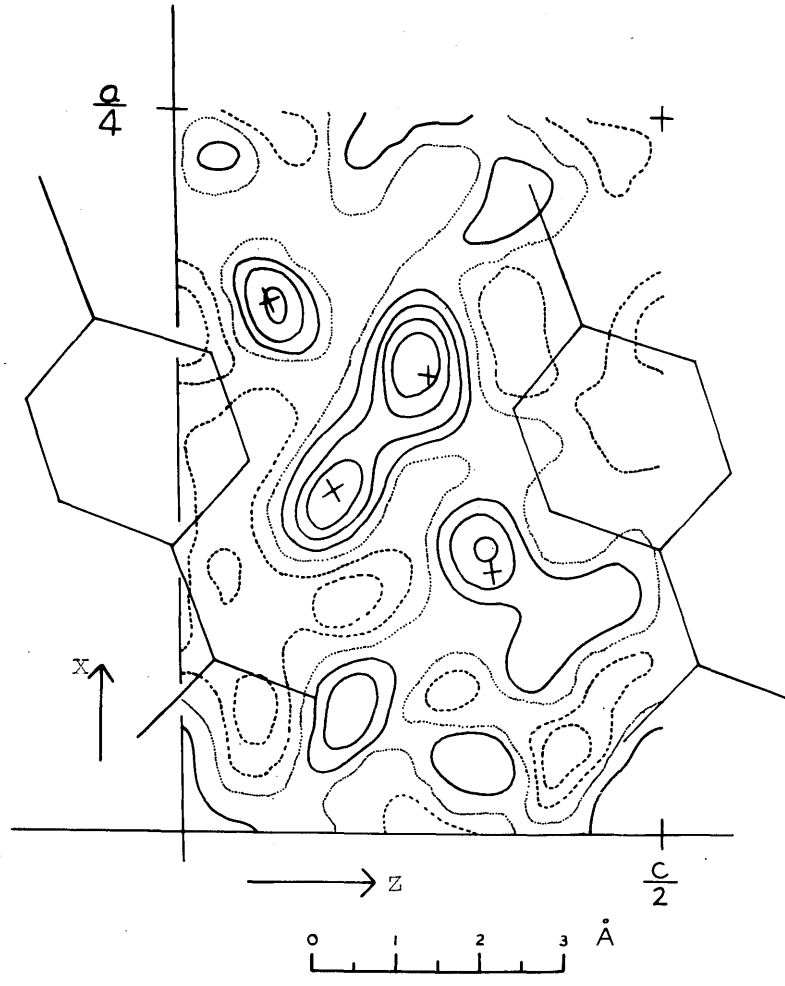


Fig.XVIII. Potassium Hydrogen Di-p-chlorobenzoate: Difference-synthesis projection on (010) to show electron distribution due to hydrogen atoms. Contour-line interval: 0.1 electrons per square Å, with zero contour shown as dotted line and negative contours as broken lines. Assumed hydrogen positions are marked by crosses.

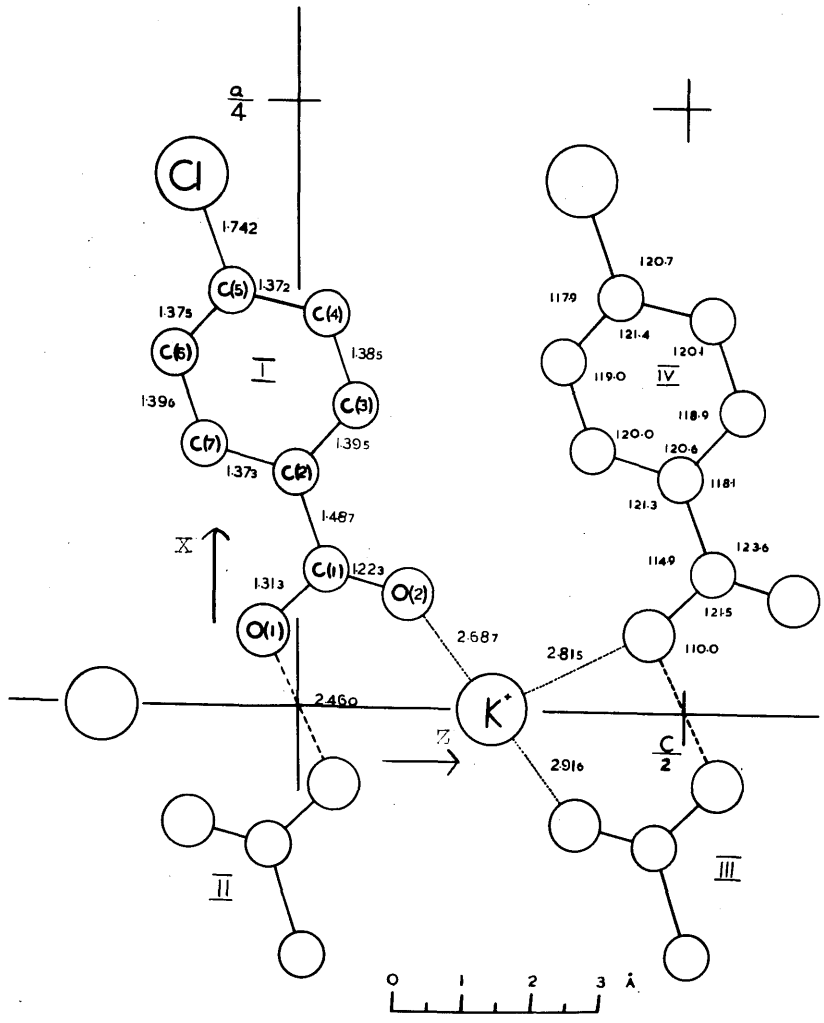


Fig. XIX. Potassium Hydrogen Di-p-chlorobenzoate: Interatomic distances (in Å) and bond angles. The numerals refer to the following positions: I (x, y, z); II ($\bar{x}$, $\bar{y}$, $\bar{z}$); III($\bar{x}$, 1+y, $\frac{1}{2}-z$); IV (x, 1-y, $\frac{1}{2}+z$).

The bond lengths and bond angles in the molecule, calculated from the coordinates given in Table 30, are shown in Table 32, Table 33 and Fig.XIX. The shorter intermolecular contacts are given in Table 34. Each potassium is surrounded by six nearest neighbours and these K .... O distances are listed in Table 35.

The standard deviations of the positional parameters, calculated by the standard way from the least-squares residuals, are listed in Table 36. From these values, the estimated standard deviation of the C - O bond is 0.013 Å, that of the C - C bond is 0.015 Å and that of the C - Cl bond is 0.012 Å; the estimated standard deviation of the bond angles is about 1^{o}. These results are calculated by the formulae given in 2.2.8.

The best plane through the chlorine and carbon atoms of the p-chlorobenzoate group, calculated by the method of Schomaker et al. (1959), has the equation,

$$0.29170\ X - 0.89642\ Y + 0.33368\ Z' - 0.26445 = 0,$$

where X, Y and Z' are in Angstrom units and are referred to the orthogonal system defined by a, b and c^{*}. The deviations of the atoms from this plane, which are listed in Table 37, show that these atoms are not planar. As C(1) and the chlorine atom are the main causes of non-planarity, planes were calculated omitting each of these

atoms in turn. The deviations of the atoms from these planes are shown in Table 37. Application of the χ^2 test gives

$$\chi^2 = \sum \Delta^2/\sigma^2(y) = 36,$$

for the plane through C(2), ..., C(7) and the chlorine atom. For the plane through C(1), ... , C(6) and C(7), the results show that

$$\chi^2 = 7.14 .$$

It is found from tables of χ^2 (Fisher and Yates, 1957) that this corresponds to a probability of less than one in a thousand in the first case and one in four in the second case that no atom deviates significantly from the calculated plane. This means that the chlorine atom and the atoms of the benzene ring must be regarded as non-coplanar whereas the evidence that C(1) is displaced out of the plane of the benzene ring is inconclusive.

The best plane through the atoms of the benzene ring has equation,

$$0.28023\ X - 0.89860\ Y + 0.33763\ Z' - 0.22724 = 0.$$

The deviations from this plane are small (Table 37) and since,

$$\chi^2 = 4.37,$$

the displacements are not significant.

The atoms of the carboxyl group and C(2) lie on the

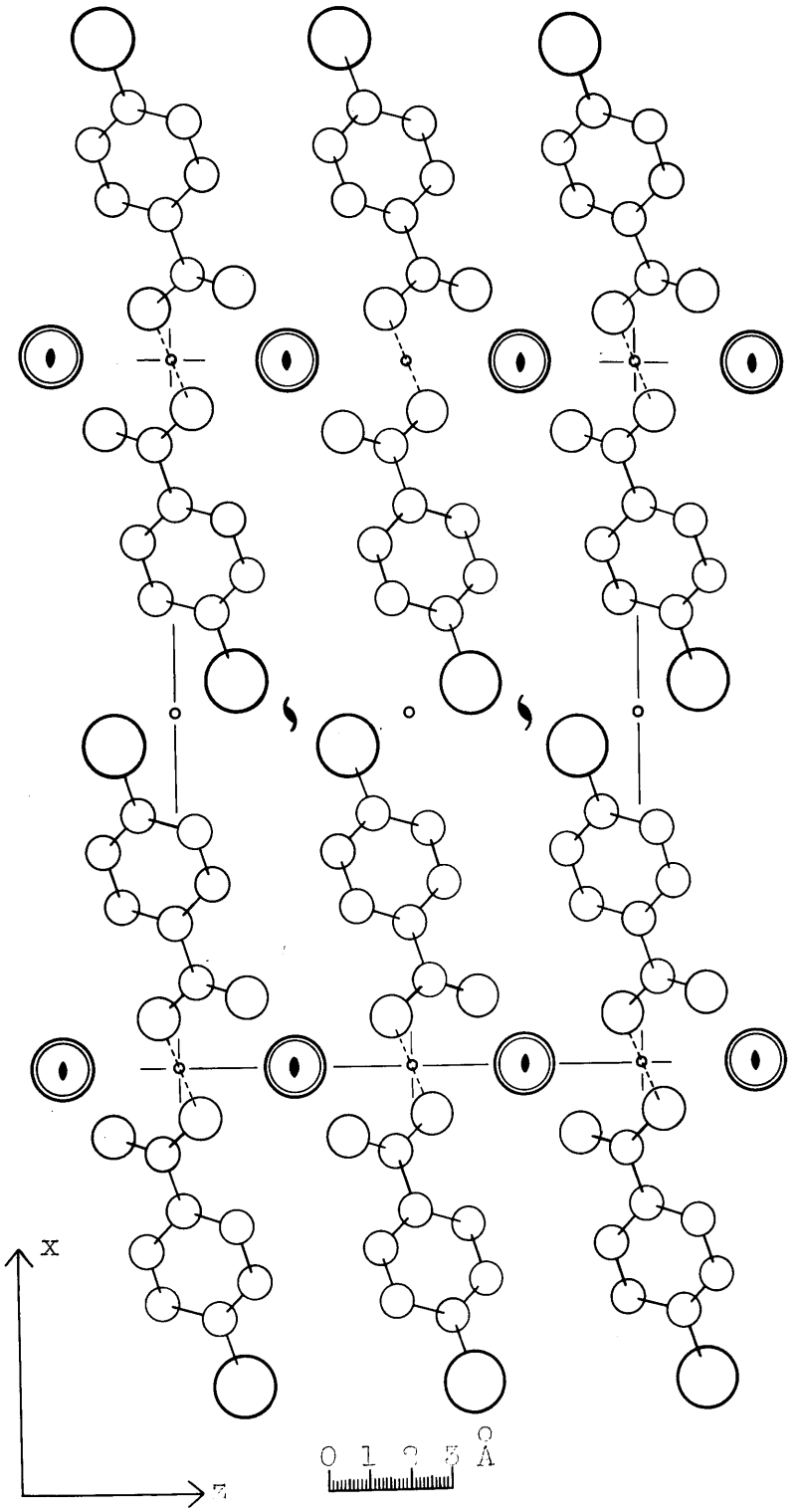


Fig.XX. Potassium Hydrogen Di-p-chlorobenzoate: Projection of part of structure on (010). For interpretation, see Fig.XIX.

plane with equation,

$$0.22698\ X + 0.95441\ Y + 0.19387\ Z' - 0.00452 = 0.$$

The angle between this plane and the plane of the benzene ring is $9^{o}18'$ and the tilt of the benzene ring with respect to the (010) plane is 26^{o}.

2.4.18. Description of the Structure.

The structure is similar to that of ammonium hydrogen dicinnamate (2.3.7.). Fig. XX shows the structure projected on to the (010) plane. The final F_o Fourier map of the (010) projection is shown in Fig.XVII. A $(F_o - F_{c'})$ map was computed using the h0ℓ data where $F_{c'}$ is the value of the structure factor calculated for the chlorine, potassium, carbon and oxygen atoms only; this is illustrated in Fig.XVIII and provides evidence of the hydrogen atoms.

2.4.19. Discussion.

This analysis establishes that the ammonium, potassium and rubidium acid salts of p-chlorobenzoic acid are isomorphous and belong to the type A acid salts. This is in agreement with the prediction made on the basis of the infrared spectra. The results of the refinement of

the potassium salt show that the hydrogen bond has length 2.460 ± 0.015 Å and joins two oxygen atoms related by a centre of symmetry.

The bond lengths and bond angles in the benzene ring and the carboxyl group compare favourably with the values obtained in similar compounds (2.2.10 and 2.3.8.). The average C - C bond length in the benzene ring is 1.383 Å. The exocyclic C(1) - C(2) bond has length 1.487 Å. This is in good agreement with the value estimated by Dewar and Schmeising (1959) for a single bond between two carbon atoms in the sp^2 state of hybridisation, 1.471 Å, and the values observed in benzoic acid, 1.48 Å (Sim, Robertson and Goodwin, 1955) and in salicylic acid, 1.458 Å (Cochran, 1953). The angle C(1) - O(1) ..... O(1)' is approximately tetrahedral which is the value expected for the formation of a strong hydrogen bond. The best plane through the carboxyl group and C(2) also includes, to a good approximation, the origin which means that the hydrogen bond lies in the plane of the carboxyl atoms. The angles round C(1) conform to the pattern normally observed in acid salts (2.2.10).

The C - Cl bond has length, 1.742 Å. This compares well with the values found in o-chlorobenzoic acid, 1.737 Å (Ferguson and Sim, 1961) and 4,4'-Dichlorodiphenyl sulphone,

1.736 Å. (Sime and Abrahams, 1960). All these values are less than the mean C - Cl distance in aliphatic compounds, 1.767 ± 0.002 Å (Tables of Interatomic Distances, 1958) by an amount equal to the expected decrease in the radius of the carbon atom on changing from sp^3 to sp^2 hybridisation.

The intermolecular contacts between chlorine atoms related by the centres of symmetry at $(\frac{1}{4},\frac{1}{4},0)$ and $(\frac{1}{4},\frac{3}{4},0)$ and the screw axis are 3.68 Å, 4.08 Å and 3.58 Å respectively. These distances are in agreement with the van der Waals radius for chlorine, 1.80 Å (Pauling, 1960 : Table 7.20). The unexpected feature of the structure is the displacement of the chlorine atom from the mean plane of the benzene ring. The out-of-plane bending of the C - Cl bond is about 4°. If a position is assumed for the chlorine atoms on the plane of the benzene ring, the distance between the two chlorine atoms related by the centre of symmetry at $(\frac{1}{4},\frac{1}{4},0)$ now becomes 3.49 Å which is much shorter than twice the van der Waals radius for chlorine. This rather suggests that the out-of-plane bending of the C - Cl bond allows the chlorine atoms to stack along the planes at $x = \frac{1}{4}$ and $x = \frac{3}{4}$ without any unusually short intermolecular contacts. The amount

of energy, V, required to bend the C - Cl bond out of the plane is given by

$$2V = F\theta^2 ,$$

where F is the appropriate force constant and θ is the angle between the C - Cl bond and the plane. If a value of 5×10^{-12} ergs $rad.^{-2}$ is estimated for F (Brand, 1962), the value of V is about 200 $cals.mole^{-1}$ Thus the energy required to bend the C - Cl out of the plane of the benzene ring is small and is considerably less than the energy gained in the close packing of the carboxyl groups and the potassium ions at the other end of the molecule. Deviations from planarity have been observed in other molecules, which ought theoretically to be planar. In anthracene (Cruickshank, 1956) and 2:3-8:9 dibenzoperylene (Lipscomb, Robertson and Rossmann, 1959), the molecules are buckled in such a way that closer packing occurs and it is postulated that the energy of strain in distorting the molecules is less than the energy gained by the closer packing.

The potassium ion is surrounded by six oxygen atoms at the corners of a distorted octahedron at a mean distance of 2.81 Å (Table 35). This is the normal coordination observed in potassium acid salts and the average K .... O distance is in good agreement with the average distances

observed in potassium hydrogen bisphenylacetate, 2.83 Å, potassium hydrogen dibenzoate, 2.81 Å and potassium hydrogen di-p-nitrobenzoate, 2.74 Å. In the dipotassium salt of methylene-bis-nitrosohydroxylamine (Bryden, 1959) and potassium dithionate (Stanley, 1956), the potassium ions are again surrounded by six oxygen atoms at mean distances of 2.81 Å and 2.83 Å, respectively. In potassium hydrogen maleate (Darlow and Cochran, 1961) and potassium aminedisulphonate (Jeffrey and Jones, 1956), the coordination has increased to eight and nine with an average distance of 2.90 Å in both cases. This illustrates the expected increase in average K .... O distance as the coordination number increases.

Finally, it is interesting to note that Bryden and McCullough (1956) used coordinates obtained in a study of benzeneseleninic acid (Bryden and McCullough, 1954) as the starting point in the study of p-chlorobenzeneseleninic acid. The relationship between benzeneseleninic acid and various para- substituted benzeneseleninic acids is very similar to that between potassium hydrogen dibenzoate and potassium hydrogen di-p-chlorobenzoate.

SECTION 5. FINAL DISCUSSION.

Table 38 gives a list of the acid salts whose structures have been determined. In Section 1, the acid salts which possess a crystallographically symmetrical hydrogen bond, are listed, i.e. type A. They all exhibit the anomalous spectra characteristic of this type. (Hadzi and Novak, 1960.) In almost all these acid salts, the space group is not unambiguously determined by the absences and the centred space group has been chosen on the grounds that a successful analysis results on the basis of it (e.g. 2.4.5.). In these cases, if the choice of the centred space group is wrong, then the evidence for symmetry in the hydrogen bond would fail. In every case, there remains the possibility that in each individual hydrogen bond the hydrogen is nearer to one or other of the oxygen atoms but the bonds are statistically disordered so that, overall, the bonds appear to be symmetrical.

Section 2 of Table 38 lists the acid salts which do not contain a symmetrical hydrogen bond. These are acid salts of type B and do not show the spectral anomaly.

Several of the acid salts in Section 1 have been the subject of neutron-diffraction studies, viz. potassium hydrogen bisphenylacetate (Bacon and Curry, 1957),

TABLE 38.

Crystal Structures of, and Hydrogen Bonding in Acid Salts.

SECTION 1.

ACID	METAL	SPACE GROUP	HYDROGEN BOND	
			Symmetry	Length(Å)
Phenylacetic	K	I2/a	$\bar{1}$	2.55±0.05 (1)
p-OH-benzoic*	K	P2/c	$\bar{1}$	2.61±0.04 (2)
Benzoic	K	C2/c	$\bar{1}$	2.51±0.04 (3)
Cinnamic	NH_4	I2/a	$\bar{1}$	2.509±0.015 (4)
o-NO_2-benzoic	Rb	P$\bar{1}$	$\bar{1}$	2.43±0.06 (5)
p-Cl-benzoic	K	C2/c	$\bar{1}$	2.460±0.015 (4)
Acetic	Na	Ia3	2	2.444±0.010 (4)
Carbonic*	Na	C2/c	$\bar{1}$	2.53±0.02 (6)
Maleic	K	Pbcm	m	2.437±0.004 (7)

SECTION 2.

Salicylic*	NH_4	$P2_1/c$	-	- (8)
p-NO_2-benzoic	K	P$\bar{1}$	-	2.492±0.020 (5)
o-phthalic	NH_4	Pcab	-	- (9)

* Salt is hydrated.

TABLE 38.(Cont'd)

References.

(1) Speakman (1949).

(2) Skinner and Speakman (1951).

(3) Skinner, Stewart and Speakman (1954).

(4) This Thesis.

(5) Shrivastava and Speakman (1961).

(6) Brown, Peiser and Turner-Jones (1949).

(7) Darlow and Cochran (1961).

(8) Downie and Speakman (1954).

(9) Okaya and Pepinsky (1957).

sodium sesquicarbonate (Bacon and Curry, 1956) and potassium hydrogen maleate (Peterson and Levy, 1958). Recently, Bacon and Curry (1960) have concluded from studies of potassium hydrogen bisphenylacetate at 120°K that the acidic hydrogen takes part in a centred hydrogen bond.

Thus, the results from X-ray crystallography, infrared spectroscopy and neutron diffraction all suggest that the hydrogen bond in type A acid salts is truly symmetrical.

CHAPTER 3.

THE CRYSTAL STRUCTURE OF

N-α-PICOLINE OXIDE HEMIHYDROBROMIDE.

THE STRUCTURE OF N-α-PICOLINE OXIDE HEMIHYDROBROMIDE.

3.1. Introduction.

The oxidation of pyridine to give pyridine N-oxide was first performed by Meisenheimer (1926) using perbenzoic acid. This made available a complete range of compounds from substituted pyridines; the details of a preparation of N-α-picoline oxide are given by Ishikawa and Zai-Ren (1943).

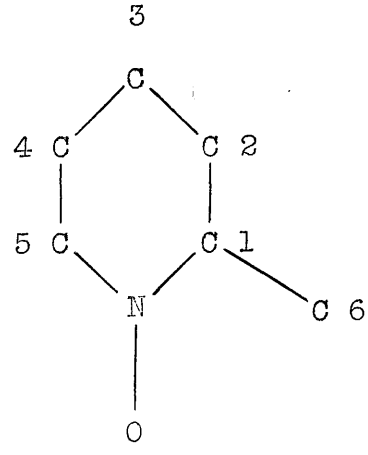
Like amine-oxides in general, e.g. $R_3N \rightarrow O$, the pyridine N-oxides have some basic properties and are capable of forming hydrochlorides, e.g. $R_3NOH^+Cl^-$. In this case, two molecules of N-α-picoline oxide and one molecule of hydrobromic acid have combined to give a stable compound which is the basic analogue of the acid salts of Chapter 2. For this reason, it will be treated in this discussion as a molecule of twice the molecular weight implied in the name.

The main features of interest in this compound are the location of the hydrogen associated with the bromide ion and the type of hydrogen bonding involved. This study was undertaken at the suggestion of Dr. Hadzi who had noticed that this compound had an infrared spectrum which

was not related to those normally given by pyridine N-oxides.

An infrared spectrum of this compound in nujol was prepared from the sample provided by Hadzi. The main feature of the spectrum is the bands of absorption between 1500 - 1300 $cm.^{-1}$ and below 1140 $cm.^{-1}$ with a break at 840 $cm.^{-1}$ In N-picoline oxide, the absorption bands of the N - O group normally occur at 1270 $cm.^{-1}$ Strong electron donors lower this and in N-α-picoline oxide, the absorption is at 1264 - 1260 $cm.^{-1}$ (Bellamy, 1958). In the spectrum of N-α-picoline oxide hemihydrobromide, there are no strong peaks in this region apart from the "plateau" of general absorption. The occurrence of these bands of absorption and the lack of a peak attributable to the N - O group suggest that the N - O group is modified by the hydrogen bond in a similar way to the carboxyl group of the acid salts.

The numbering system used is shown below:-



3.2. Experimental.

A sample of N-α-picoline oxide hemihydrobromide was supplied by Hadzi and crystals suitable for the X-ray investigation were obtained by recrystallisation from acetone. The crystals formed plates showing straight extinction. Infrared spectra of the original sample and the recrystallised material were compared and are identical except for a small peak at 3300 $cm.^{-1}$ in the original sample's spectrum which is probably caused by water from the atmosphere and a peak at 1730 $cm.^{-1}$ in the recrystallised material's spectrum. The latter peak could be caused by acetone of crystallisation but this is unlikely as the intensity of absorption is weak. Powder photographs of the two samples were prepared; these are identical. The absence of acetone of crystallisation is proved and the analysis proceeded on this basis.

The cell dimensions were obtained from rotation, oscillation and Weissenberg photographs about the unique axis. Intensity data for the h0ℓ, h1ℓ, h2ℓ, h3ℓ, h4ℓ and h5ℓ lattice nets were recorded on an equi-inclination Weissenberg camera; of these, only the h0ℓ and h3ℓ data have been used in this analysis.

A second crystal was mounted about an axis which proved to be the diagonal of the C- face and Weissenberg photographs of the hhℓ net were taken. The density was obtained by the method of flotation in carbon tetrachloride and dioxan.

The intensity data were measured visually using the multiple film technique (Robertson, 1943) and converted to structure amplitudes by application of the usual corrections. The number of data available was 118 in hoℓ, 184 in hhℓ and 210 in h3ℓ. No absorption corrections were applied and Cu Kα radiation was used throughout.

3.3. Crystal Data.

The crystal data for N-α-picoline oxide hemihydrobromide are shown below :-

$(C_6NOH_7)_2HBr$ M = 299.18

Monoclinic a = 13.12 ± 0.05

b = 6.89 ± 0.02

c = 14.74 ± 0.05

$\beta = 103^{\circ}\ 3' \pm 30'$

Volume of unit cell = 1298 $\mathring{A}^3$

ρ obs. = 1.52 ; calculated on the basis of 4 molecules in the unit cell, ρ = 1.531.

F(000) = 608.

Absorption coefficient for X-rays ($\lambda = 1.542$ Å) is 45.2cm.$^{-1}$

Absent Spectra : (hkℓ) $h + k = 2n + 1$

(hOℓ) $\ell = 2n + 1$

(OkO) $k = 2n + 1$

Space Group : $C\,2/c$ — C_{2h}^6 or Cc — C_s^4

3.4. Space Group.

The space group is not determined uniquely by the absences but, on the experience of work on the acid salts, it was assumed to be $C\,2/c$. This has been justified by the successful outcome of the analysis.

As there are eight equivalent positions in the space group and four molecules in the unit cell, the bromide ion and its associated hydrogen atom are sited on one of the twofold special positions of the space group. The positions available are the twofold axis and centres of symmetry.

3.5. The (010) Projection.

The plane group of the (010) projection is p2 and the bromide ion will project on to a centre of symmetry which may be taken as the origin. The hOℓ data were used in a Patterson synthesis. In the Patterson projection, the Br - Br vector will occur in the origin; the vectors between the bromide ion and each of the other atoms in turn

will be larger than any other interatomic vectors and an image of the structure will be apparent. The Patterson projection is shown in Fig.XXI. This is interpreted in terms of a six-membered ring lying almost perpendicular to the (010) plane and inclined at about 25° to the c- axis. The large unitary structure factor, 0.61, of the $(40\bar{2})$ is in agreement with this interpretation of the Patterson projection.

Positions were assigned to the atoms and structure factors calculated using an isotropic temperature factor of $B = 3\ \text{Å}^2$. The Freeman (1959) scattering factor curves for oxygen, nitrogen and carbon were employed; the values given by Thomas and Umeda (1957) for a bromine atom were used. The f- curve for the bromine atom was reduced to half-scale to allow for the effect of the ion being sited on the centre of symmetry. An attempt to distinguish the oxygen and nitrogen atoms was made on the assumption that N - O groups would be the nearest neighbour of the bromide ion. In projection, the fully resolved peak away from the ring appears the nearest atom to the bromide ion and this was thought to be the oxygen atom. This assumption was later proved to be wrong. The initial value of the discrepancy was 26.2% and this was reduced

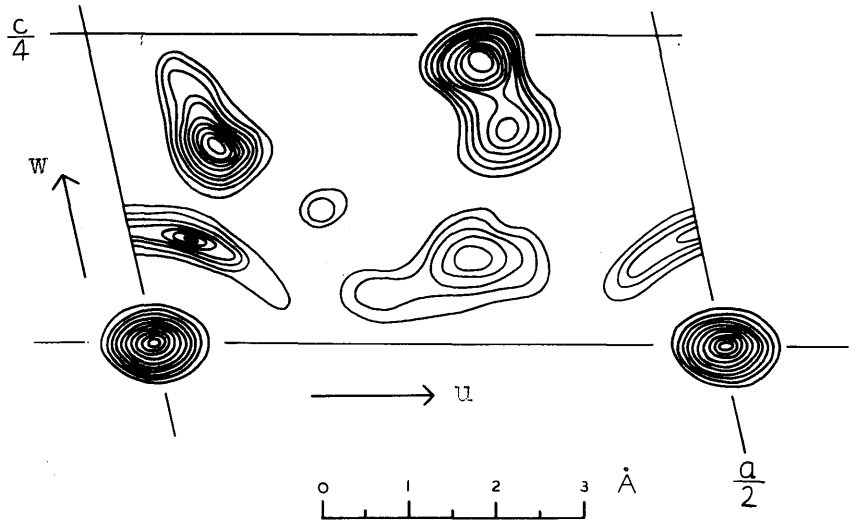


Fig.XXI. N-∝-Picoline Oxide Hemihydrobromide: Patterson (010) projection, P(uw). Contours are at equal but arbitrary intervals except at origin.

TABLE 39.

N-α-Picoline Oxide Hemihydrobromide:

Atomic Coordinates from (010) Projection.

Coordinates x and z are referred to the monoclinic axes and are expressed as fractions of the axial lengths. Origin is at the bromide ion.

Atom	x	z
Br	0.000	0.000
O	0.328	0.228
N	0.340	0.228
C(1)	0.333	0.182
C(2)	0.362	0.183
C(3)	0.423	0.303
C(4)	0.417	0.348
C(5)	0.400	0.343
C(6)	0.287	0.078

(When origin is shifted to (0, 0, $\overline{0.25}$), these coordinates correspond to molecule III in Fig. XXV.)

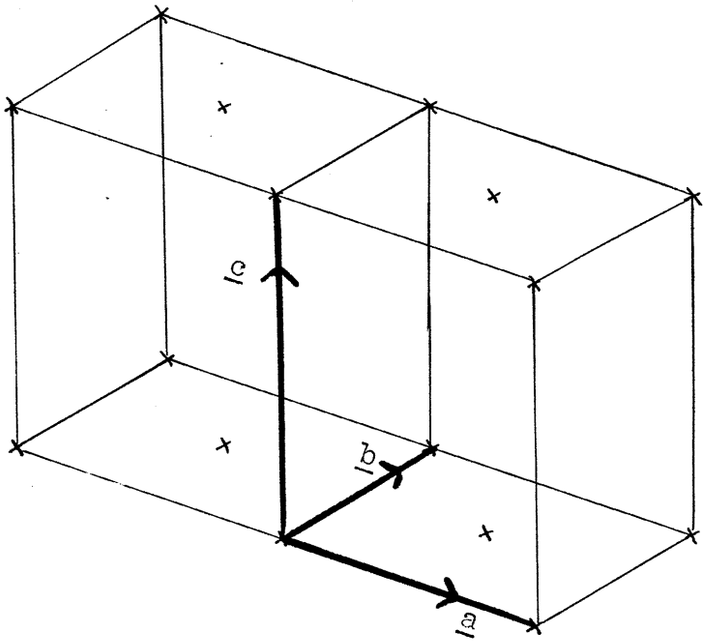
to 21% by Fourier refinement of the positional parameters. The very extensive overlap made further refinement difficult and of doubtful value once the inclination of the ring had been determined.

The final coordinates are shown in Table 39; the position of the bromide ion is taken as the origin and the assignment of the chemical type is that finally determined. When the origin is shifted to $(0,0,\overline{0.25})$, these coordinates correspond to molecule III in Fig.XXV.

3.6. The C-Face Diagonal Projection.

As the other two axes are of length ~ 14 Å, the use of one of the other two projections to give the y-coordinates was impossible.

Fig.XXII shows the lattice in which this compound crystallises. It is normally described in terms of a face-centred monoclinic unit cell defined by the three vectors a, b and c. Alternatively, it can be described in terms of a triclinic cell given by a', b' and c' (c' is identical with c). The monoclinic unit cell requires four parameters, a, b, c and β whereas the triclinic cell formally requires six parameters a', b', c', α', β' and γ'. As they both describe the same lattice, only four of the



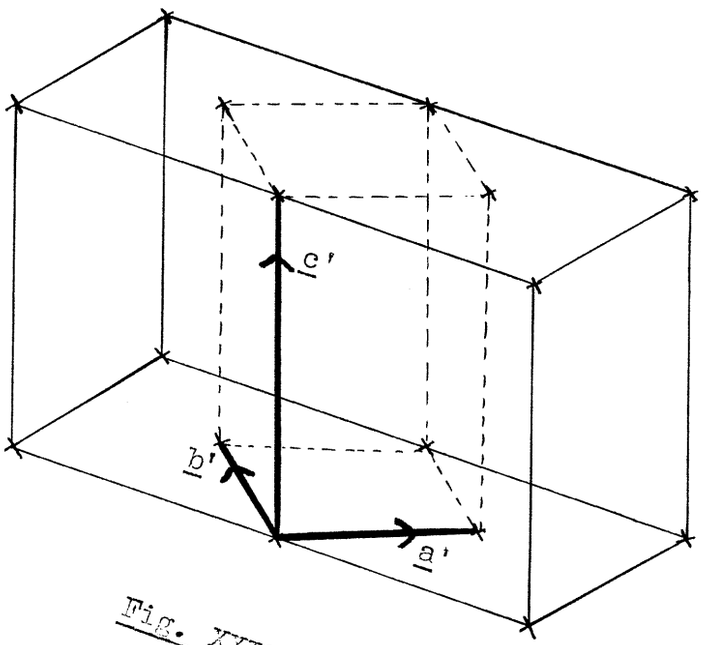


Fig. XXII.

triclinic parameters can be independent. The calculated dimensions of this pseudo-triclinic unit cell are shown in Table 40.

TABLE 40.

a'	= 7.41 Å	α'	= 78° 34'
b'	= 7.41	β'	= 101° 26'
c'	= 14.72 (≡ c)	γ'	= 124° 36'

The dimension of the b'- axis (the diagonal of the C-face of the monoclinic cell) suggests that the projection down this axis could be used to give a' and c'- coordinates.

In the monoclinic system, the space group is $C^{2}/_{c}$ which has eight equivalent positions. Of these, four arise from the face-centring. The remaining four can be obtained from (1) the operation of the twofold axis at $(0, y, \frac{1}{4})$ on a basic point (x, y, z) to give $(\bar{x}, y, \frac{1}{2}-z)$ and (2) the operation of a centre of symmetry at the origin on both points to give $(\bar{x}, \bar{y}, \bar{z})$ and $(x, \bar{y}, \frac{1}{2}+z)$. The face-centring is no longer present in the triclinic cell which has half the volume of the monoclinic cell. When the transformation is made, the centres of symmetry are retained at the origin but the twofold axis relationship is destroyed, i.e. the points (x, y, z) and $(\bar{x}, y, \frac{1}{2}-z)$ will transform into unrelated points. The number of equivalent positions in the pseudo-

triclinic cell is therefore 2 and the space group is $P\bar{1}$. As this cell will contain two units of $C_{12}N_2O_2H_{15}Br$, the bromide ion no longer occupies a special position.

The data contained in the Weissenberg photograph taken when the crystal is rotated about the face-diagonal were indexed in terms of the triclinic cell to give h'0ℓ' data. The Patterson projection P(u'ow') was computed using these data and the resulting map is shown in Fig. XXIII.

As the bromide ions occupy the positions (x,y,z) and ($\bar{x}$,$\bar{y}$,$\bar{z}$), the Br - Br vectors occur at (2x,2z) and (2$\bar{x}$,2$\bar{z}$). The highest peak outside the origin occurs at (0.25, 0.50) with height of 790 in arbitrary units; the next highest peak is 397. This establishes the bromide ion to be (0.125, 0.25). The function obtained by the superposition of one Patterson function with its origin at one of the positions of the bromide ions (0.125, 0.25) on another Patterson function with its origin at the position of the other bromide ion (0.$\overline{125}$, 0.$\overline{25}$) is shown in Fig.XXIV. After a consideration of the type of overlap to be expected in this projection from a knowledge of the b-axis projection, Fig.XXV, the pyridine rings could be identified. Fig.XXVI gives a diagram of this projection. Structure factors calculated for the h'0ℓ' data using coordinates obtained from the superposition Patterson

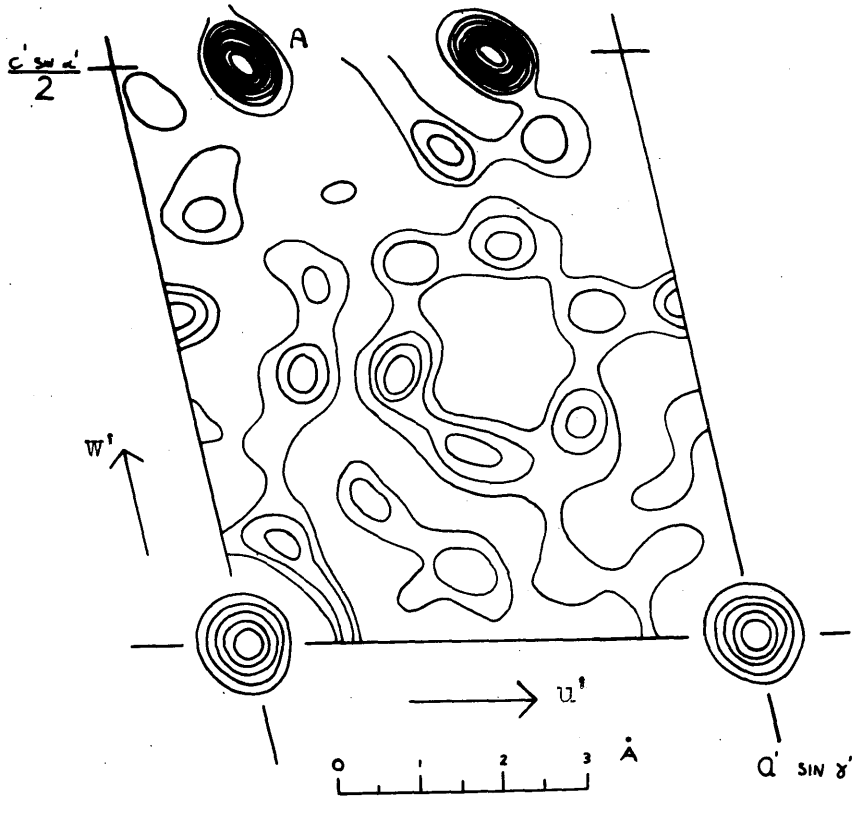


Fig.XXIII. N-∝-Picoline Oxide Hemihydrobromide: Patterson projection along the C- face diagonal, P(u'w'). Contours are at equal but arbitrary intervals except at origin.

TABLE 41.

N-α-Picoline Oxide Hemihydrobromide:

Atomic Coordinates from (110) Projection.

Coordinates x' and z' are referred to the triclinic axes and are expressed as fractions of the axial lengths. Origin at centre of symmetry.

Atom	x'	z'
Br	0.129	0.250
N	0.400	0.487
O	0.558	0.460
C(1)	0.237	0.419
C(2)	0.095	0.447
C(3)	0.069	0.528
C(4)	0.225	0.598
C(5)	0.393	0.563
C(6)	0.265	0.325
N'	0.727	0.030
O'	0.907	0.036
C(1)'	0.580	0.100
C(2)'	0.376	0.080
C(3)'	0.300	0.001
C(4)'	0.420	-0.083
C(5)'	0.627	-0.067
C(6)'	0.676	0.183

had a discrepancy of 19.9%. One cycle of Fourier refinement followed and the final atomic coordinates are shown in Table 41; the unprimed atoms correspond to the molecule drawn in dashed lines at c' = $\frac{1}{2}$ and the primed atoms correspond to the molecule drawn in full lines at c' = 0 in Fig.XXVI.

3.7. Three-Dimensional Structure.

The structure has been determined in two projections and the three-dimensional structure can be obtained by combining these results.

Fig.XXVII shows a section of the lattice with the vectors describing the two unit cells inserted. c (and c') is inclined at some angle, β, to the vector a and is perpendicular to the vector b.

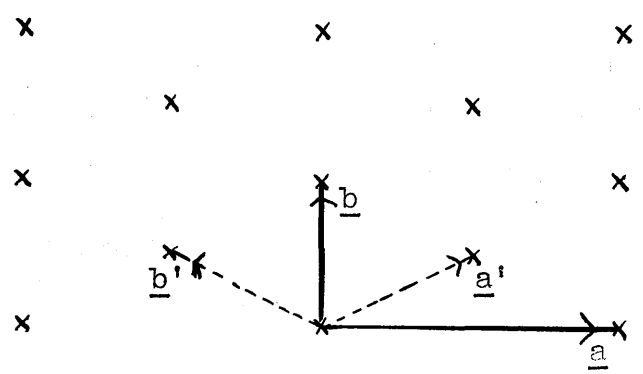


Fig.XXVII.

In vector notation,

$$\underline{a} = \underline{a}' - \underline{b}'$$
$$\underline{b} = \underline{a}' + \underline{b}' \qquad \text{i.e.}$$
$$\underline{c} = \underline{c}'$$

Monoclinic → Triclinic

$$\begin{bmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

If any point, P, $\underline{v}$ has coordinates (x y z) in the monoclinic system (unprimed), then

$$\underline{v} = x\underline{a} + y\underline{b} + z\underline{c}$$
$$= x(\underline{a}' - \underline{b}') + y(\underline{a}' + \underline{b}') + z\underline{c}'$$
$$= (x + y)\underline{a}' + (y - x)\underline{b}' + z\underline{c}' .$$

If the coordinates of P in the triclinic cell are (x'y'z'), then

$$x' \equiv x + y, \quad y' \equiv y - x, \quad z' \equiv z.$$

The values of x and z have been determined from the (010) projection and x' and z' from the (110) projection. This enables the y- coordinate to be calculated from

$$x' \equiv x + y ;$$

$$\text{i.e.} \quad y = x' - x.$$

The origin of the b- axis projection was shifted to $(0,0,\overline{0.25})$ to make the z- coordinate of the bromide ion correspond in Table 39 and Table 41. The y- coordinates were calculated from the above relationship using the coordinates in Table 39 and the coordinates of the unprimed atoms in Table 41. The three-dimensional coordinates obtained are shown in Table 42. Structure

factors, calculated for the h3ℓ net, gave a R value of 23%.

The diagonal projection data were reindexed in terms of the monoclinic cell. A three-dimensional Fourier synthesis was computed using the data for the h0ℓ, hhℓ and h3ℓ nets and new coordinates obtained.

From the peak heights in the F_o map, it was realised that the assignment of chemical type was wrong and structure factors were calculated treating all the atoms as carbon atoms. The value of R improved by 2% on all the nets. The values of R, after a second cycle of Fourier refinement, are 17.1%, 18.0% and 18.6% for the h0ℓ, hhℓ and h3ℓ nets respectively. Table 43 lists the observed structure amplitudes and the structure factors calculated at this stage of refinement.

3.8. Description of the Structure.

The coordinates of the atoms at this stage of the analysis are shown in Table 44; they refer to molecule I in Fig. XXV. The assignment of chemical type was made from the peak heights in the Fourier map, the bond lengths and the packing of the pyridine rings. The bond lengths and bond angles, calculated from the coordinates given in Table 44, are shown in Table 45.

TABLE 42.

N-α-Picoline Oxide Hemihydrobromide:

Initial Three-Dimensional Atomic Coordinates.

Coordinates x, y and z are referred to the monoclinic axes and are expressed as fractions of the axial lengths. Origin is at centre of symmetry on c glide plane.

Atom	x	y	z
Br	0.000	0.129	0.250
O	0.328	0.230	0.478
N	0.340	0.060	0.478
C(1)	0.333	-0.096	0.432
C(2)	0.362	-0.267	0.433
C(3)	0.423	-0.354	0.553
C(4)	0.417	-0.192	0.598
C(5)	0.400	-0.007	0.593
C(6)	0.287	-0.022	0.328

TABLE 43.

N-∝-Picoline Oxide Hemihydrobromide.

h	k	ℓ	$\|F_o\|$	F_c
0	0	2	62	59
		4	112	134
		6	119	- 110
		8	48	38
		10	65	- 48
		12	72	55
		14	58	- 44
		16	33	19
		18	24	- 24
2	0	0	60	66
		2	118	- 129
		4	78	83
		6	146	- 148
		8	68	54
		10	69	- 45
		12	51	38
		14	41	- 24
		16	24	18
	-	2	90	- 108
	-	4	84	94
	-	6	75	- 76
	-	8	115	122
	-	10	65	- 62
	-	12	58	37
	-	14	44	- 36
	-	16	34	23
	-	18	17	- 10
4	0	0	57	- 34
		2	94	- 101
		4	131	120
		6	73	- 71
		8	81	76
		10	68	- 46
		12	54	48
		14	31	- 20
		16	22	21
	-	2	240	- 330
	-	4	6	20
	-	6	92	- 96
	-	8	67	72
	-	10	65	- 58
	-	12	27	12
	-	14	61	- 54
	-	16	34	38
	-	18	22	- 18
6	0	0	104	95
		2	68	- 80
		4	104	106
		6	46	- 42
		8	54	41
		10	42	- 35
		12	30	25
		14	23	- 19
	-	2	57	- 63
	-	4	86	83
	-	6	49	- 50
	-	8	63	59
	-	10	63	- 66
	-	12	38	38
	-	14	27	- 21
	-	16	25	29
	-	18	21	- 18
8	0	0	54	56
		2	94	- 86
		4	14	8
		6	72	- 68
		8	42	37
		10	45	- 37
		12	24	19
		14	12	- 15
	-	4	118	131
	-	6	46	- 58
	-	8	54	46
	-	10	40	- 45
	-	12	50	42
	-	16	36	- 42
	-	18	12	14
10	0	0	51	61
		2	56	- 56
		4	27	20
		6	42	- 31
		8	22	20
		10	37	- 25
		12	11	14
	-	2	50	- 51
	-	4	39	46
	-	6	57	- 47
	-	8	31	28
	-	10	41	- 36
	-	12	24	29
	-	14	36	- 44
	-	16	9	8
12	0	0	48	47
		2	8	- 12
		4	36	43
		6	19	- 27
		8	21	23
	-	2	25	- 30
	-	4	14	18
	-	6	37	- 47
	-	8	31	31
	-	10	15	- 17
	-	12	21	29
	-	14	25	- 32
14	0	0	22	28
		2	11	- 15
		4	17	22
		6	9	- 9
	-	2	19	- 27
	-	4	19	26
	-	6	19	- 30
	-	8	16	22
	-	10	16	- 18
16	0	0	9	12
		2	17	- 22
	-	2	14	26
	-	4	8	- 12
	-	6	10	15

h	k	ℓ	$\|F_o\|$	F_c
0	0	2	63	59
		4	118	134
		6	129	- 110
		8	50	38
		10	66	- 48
		12	66	55
		14	40	- 44
		16	22	19
		18	16	- 24
1	1	0	5	9
		1	85	- 115
		2	77	68
		3	135	115
		4	76	70
		5	26	- 32
		6	21	- 22
		7	108	78
		8	96	78
		9	37	- 20
		10	58	- 54
		11	46	49
		12	25	25
		13	17	- 13
		14	21	- 22
		15	21	20
		16	14	16
		17	18	- 21
		18	5	4
	-	1	62	40
	-	3	70	- 83
	-	4	96	115
	-	5	80	87
	-	6	79	- 89
	-	7	45	- 33
	-	8	37	39
	-	9	45	36
	-	10	66	- 66
	-	11	71	- 65
	-	13	15	9
	-	14	40	- 37
	-	15	21	- 25
	-	16	13	14
	-	17	17	16
	-	18	14	- 17
2	2	0	22	- 23
		1	125	- 130
		2	35	19
		3	93	41
		4	72	48
		5	117	- 108
		6	7	8
		7	70	58
		9	39	- 33
		10	18	- 18
		11	53	60
		12	24	- 27
		13	32	- 28
		15	22	24
		17	17	- 17
	-	1	89	111
	-	2	29	13
	-	3	146	- 170
	-	4	42	- 31
	-	5	31	33
	-	6	45	- 34
	-	7	91	- 105
	-	9	42	48
	-	11	41	- 34
	-	12	15	15
	-	13	44	- 44
	-	14	12	15
	-	15	25	- 29
	-	17	14	20
3	3	0	21	- 20
		1	12	12
		2	67	89
		3	78	68
		4	49	- 43
		5	43	- 39
		6	45	33
		7	45	39
		8	51	- 50
		9	46	41
		10	43	35
		11	24	25
		12	13	- 15
		13	21	- 15
		14	16	14
		15	15	14
		16	12	- 12
	-	1	80	69
	-	2	81	77

h	k	ℓ	$\|F_o\|$	F_c
3	3	- 3	83	- 65
		- 2	96	- 81
		- 1	55	51
		0	79	81
		1	56	51
		2	87	- 93
		3	32	41
		4	26	29
		5	28	- 27
		6	23	21
		7	14	10
		8	19	24
		9	17	- 22
		10	6	4
		11	10	15
		12	75	78
4	4	0	21	- 15
		1	56	58
		2	72	- 57
		3	10	10
		6	70	60
		7	23	22
		8	28	- 25
		9	11	12
		10	36	34
		12	25	- 20
		14	16	15
	-	1	10	4
	-	2	23	34
	-	3	23	29
	-	4	74	- 84
	-	5	22	22
	-	7	40	46
	-	8	40	- 52
	-	10	25	40
	-	11	9	- 22
	-	12	27	- 37
	-	14	14	10
	-	16	14	- 28
5	5	0	36	- 28
		1	19	23
		2	34	38
		3	39	- 28
		4	30	32
		5	32	32
		6	18	14
		7	32	- 27
		8	25	- 21
		9	23	23
		10	23	17
		11	12	- 11
		12	14	- 12
	-	1	38	- 35
	-	2	38	25
	-	4	47	- 37
	-	5	32	- 40
	-	6	11	10
	-	7	23	- 20
	-	8	11	10
	-	9	23	- 41
	-	10	23	21
	-	11	8	9
	-	12	10	- 16
	-	13	15	21
	-	14	7	10
6	6	0	24	- 26
		1	41	46
		2	26	- 24
		3	35	- 32
		4	8	- 6
		5	24	23
		6	24	- 30
		9	14	11
		11	24	- 21
		12	7	10
		13	11	- 17
		14	5	6
		15	7	16
		16	8	12
		17	7	- 5
		18	28	32
		19	7	25
		20	11	- 17
7	7	0	10	11
		1	20	20
		2	20	- 19
		3	14	13
		4	10	- 18
		5	15	18
		6	20	- 19
		7	15	19
		8	19	17
		9	16	- 20
		10	7	8
		11	17	20

h	k	ℓ	$\|F_o\|$	F_c
1	3	0	79	- 101
		1	77	- 85
		2	34	38
		3	46	59
		4	100	- 101
		5	50	- 49
		6	27	33
		7	69	56
		8	36	- 24
		9	33	- 19
		10	52	37
		11	35	21
		12	21	- 18
		13	30	- 25
		14	18	12
		15	18	20
		16	19	- 21
		17	17	16
	-	1	49	64
	-	2	30	21
	-	3	50	- 34
	-	4	58	- 60
	-	5	49	- 49
	-	6	53	40
	-	7	44	43
	-	8	42	- 31
	-	9	48	37
	-	10	51	44
	-	11	40	- 32
	-	12	42	- 34
	-	13	39	33
	-	14	18	18
	-	15	16	- 8
	-	16	12	- 11
	-	17	15	18
3	3	0	27	- 20
		1	14	- 12
		2	55	59
		3	73	68
		4	42	- 43
		5	36	- 39
		6	47	53
		7	33	39
		8	60	- 50
		9	56	- 41
		10	50	35
		11	34	25
		12	16	- 15
		13	20	- 15
		14	17	14
		15	15	- 14
		16	11	- 12
		17	22	29
		18	12	- 14
	-	1	38	- 35
	-	2	25	19
	-	3	64	77
	-	4	74	- 65
	-	5	41	41
	-	6	48	51
	-	7	53	- 51
	-	8	34	- 33
	-	9	52	41
	-	10	35	29
	-	11	34	- 27
	-	12	29	- 21
	-	13	19	10
	-	14	23	- 32
	-	15	21	- 22
	-	16	10	- 1
	-	17	6	15
5	3	0	21	- 34
		1	50	- 56
		2	69	83
		3	23	29
		4	22	- 26
		5	58	- 61
		6	19	15
		7	7	5
		8	53	- 46
		9	33	- 28
		10	11	7
		11	25	23
		12	26	- 21
		13	17	- 17
		14	18	20
		15	9	10
	-	1	63	67
	-	2	77	80
	-	3	52	- 49
	-	4	24	- 25
	-	5	40	41
	-	6	51	47
	-	7	31	- 27
	-	8	38	37
	-	9	42	38
	-	10	28	25
	-	11	26	- 24
	-	12	34	- 29
	-	13	24	23
	-	14	27	27
	-	15	37	- 27
	-	16	15	- 17
	-	17	13	6
7	3	0	51	- 45
		1	58	- 57

h	k	ℓ	$\|F_o\|$	F_c
7	3	2	25	35
		3	26	- 33
		4	32	- 29
		5	26	- 27
		6	37	42
		7	43	43
		8	26	- 28
		9	15	- 10
		10	10	10
		11	20	21
		12	16	- 14
		13	11	- 9
	-	1	6	7
	-	2	17	21
	-	3	58	- 50
	-	4	54	40
	-	5	43	37
	-	6	37	34
	-	7	38	- 30
	-	8	58	49
	-	9	32	33
	-	10	30	25
	-	11	27	- 30
	-	12	26	- 26
	-	13	20	22
	-	14	10	10
	-	15	9	5
	-	16	17	- 20
9	3	0	39	- 48
		1	11	- 14
		2	15	18
		3	45	47
		4	9	- 8
		5	5	0
		6	45	43
		7	23	25
		9	20	- 23
		10	21	23
		11	8	9
	-	1	32	40
	-	2	18	29
	-	3	32	- 37
	-	4	39	42
	-	5	35	- 32
	-	6	20	23
	-	7	24	- 27
	-	8	29	- 30
	-	9	21	18
	-	10	16	15
	-	11	24	- 23
	-	12	17	- 18
	-	13	15	14
	-	14	14	15
	-	15	12	- 15
	-	16	12	- 18
11	3	0	16	- 22
		1	16	- 26
		2	17	22
		3	13	15
		4	23	- 29
		5	26	- 35
		6	24	18
		7	5	1
		8	6	- 6
		9	14	- 19
	-	1	24	34
	-	2	21	28
	-	3	8	- 9
	-	4	9	17
	-	5	17	- 25
	-	6	14	17
	-	7	17	- 22
	-	8	16	- 23
	-	9	16	22
	-	10	15	- 17
	-	11	15	16
	-	12	12	- 16
	-	13	14	21
	-	14	15	19
	-	15	7	12
13	3	0	9	- 11
		1	23	- 27
		2	22	29
		3	11	- 16
		4	1	8
	-	1	14	22
	-	2	13	- 22
	-	3	15	22
	-	4	12	- 19
	-	5	13	20
	-	7	13	- 24
	-	8	11	- 17
	-	9	7	12
	-	10	10	17
	-	11	10	- 14
	-	12	5	7
	-	13	5	- 10
15	3	1	6	8
		2	8	- 16
		3	9	12
		4	11	- 16
		5	8	- 15
		6	7	11
		7	4	- 8
		8	8	5

Observed structure amplitudes and final calculated structure factors.

TABLE 44.

N-α-Picoline Oxide Hemihydrobromide:

Atomic Coordinates.

(Symbols as in Table 42.)

Atom	x	y	z
Br	0.0000	0.1248	0.2500
O	0.1789	0.7392	0.0332
N	0.1477	0.5397	0.0118
C(1)	0.1579	0.4036	0.0809
C(2)	0.1306	0.2191	0.0552
C(3)	0.0897	0.1688	-0.0312
C(4)	0.0826	0.3114	-0.1018
C(5)	0.1053	0.4961	-0.0775
C(6)	0.1997	0.4645	0.1792

TABLE 45.

N-α-Picoline Oxide Hemihydrobromide:

Bond Lengths and Bond Angles.

Atoms	Distance	Atoms	Angle
	Å		
O - N	1.45	O - N - C(1)	121°
N - C(1)	1.37	N - C(1) - C(2)	117°
C(1) - C(2)	1.35	C(1) - C(2) - C(3)	123°
C(2) - C(3)	1.31	C(2) - C(3) - C(4)	118°
C(3) - C(4)	1.42	C(3) - C(4) - C(5)	119°
C(4) - C(5)	1.34	C(4) - C(5) - N	120°
C(5) - N	1.34	C(5) - N - C(1)	122°
C(1) - C(6)	1.49	C(5) - N - O	117°
		N - C(1) - C(6)	119°
		C(2) - C(1) - C(6)	124°

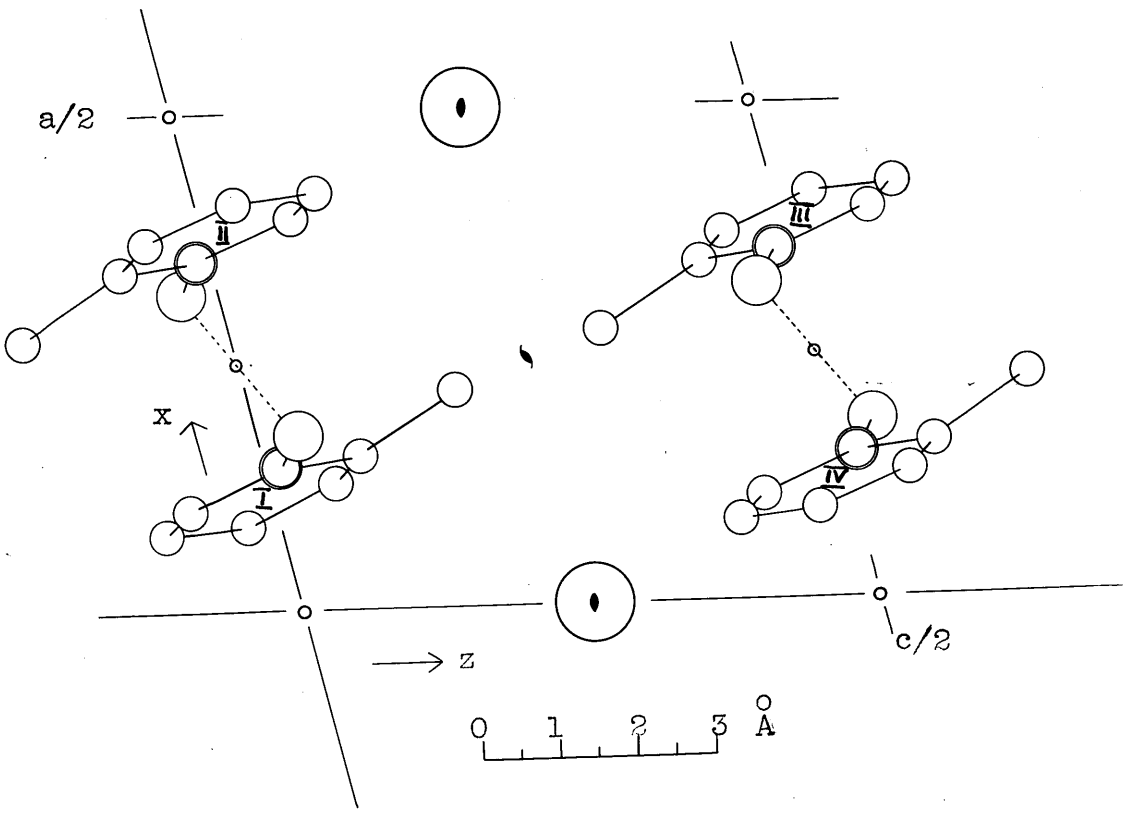


Fig.XXV. N-α-Picoline Oxide Hemihydrobromide: Projection of part of structure on (010). Large circles represent bromine and double circles represent nitrogen. The hydrogen bonds are shown as broken lines. The numerals refer to the following positions: I (x, y, z); II($\frac{1}{2}$-x, $\frac{1}{2}$-y, z); III ($\frac{1}{2}$-x, $\frac{1}{2}$+y, $\frac{1}{2}$-z); IV (x, $\bar{y}$, $\frac{1}{2}$+z).

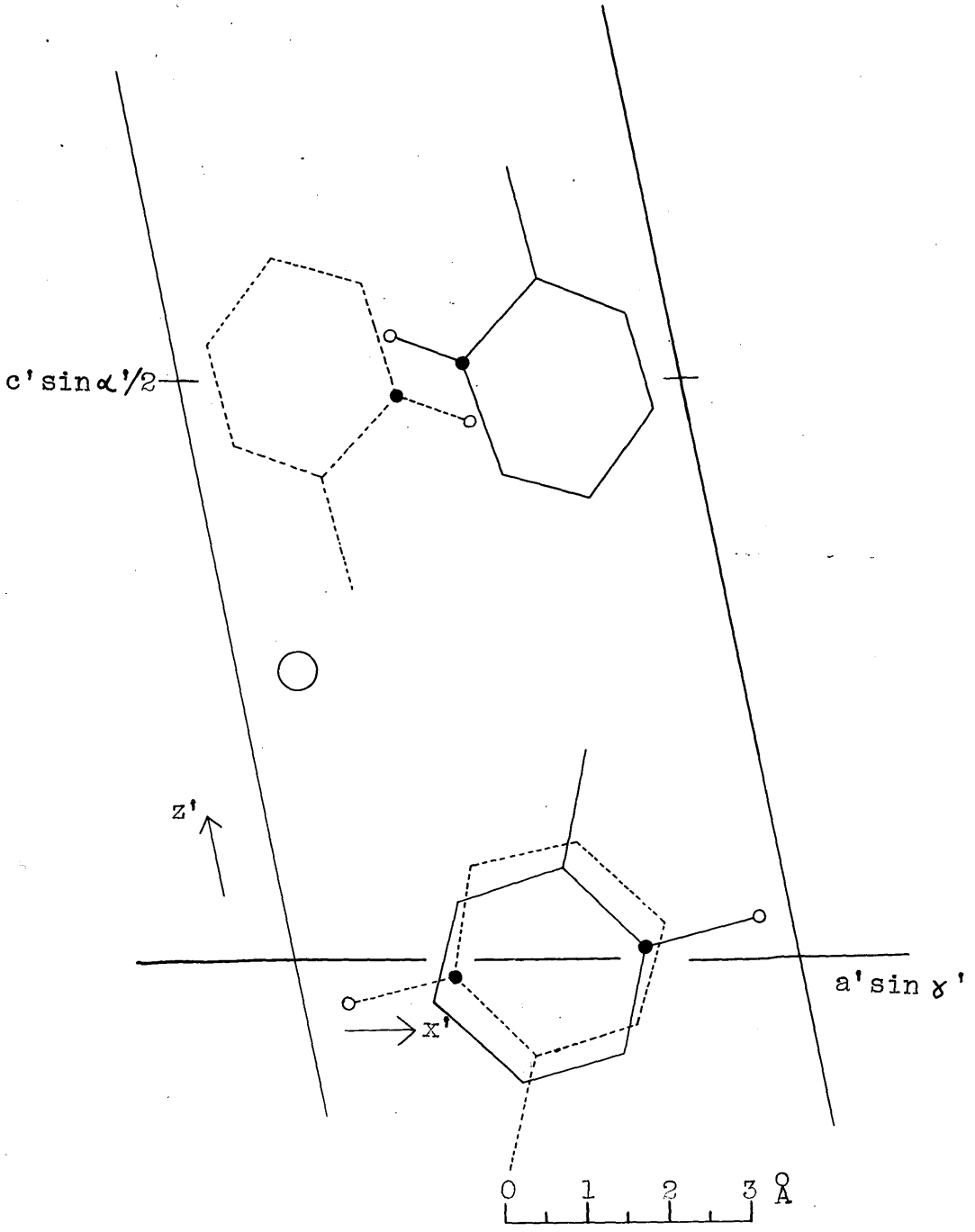


Fig.XXVI. N-α-Picoline Oxide Hemihydrobromide: Projection of part of the structure along the C-face diagonal. The large circle represents the bromide ion, the small circle represents the oxygen atom and the black circle represents the nitrogen atom.

Although the atomic coordinates have not yet been determined accurately, and the resulting bond lengths are not of great significance, the main features of the structure are clearly established. The projection of the structure on to the (010) plane is shown in Fig. XXV. The bromide ions are sited on twofold axes of symmetry. The oxygen atoms of two pyridine rings make a short intermolecular contact across the centre of symmetry at $(\frac{1}{4},\frac{1}{4},0)$; the length of the contact is 2.30 Å. As this is very much shorter than twice the van der Waals radius of oxygen, 1.4 Å, this suggests that the two oxygen atoms are involved in a symmetrical hydrogen bond, O ... H ... O. The observed length is very much less than the length of the hydrogen bonds in the acid salts, but, as the coordinates of the atoms involved were obtained from regions in the projections where there is considerable overlap, the length is, as yet, not very accurate. The methyl groups of the pyridine rings are related by the screw axis and the intermolecular contacts are over 4 Å. The bromide ion makes short contacts with the atoms of six pyridine rings. An unusual feature is that the contacts are not with the oxygen and nitrogen atoms but with the carbon atoms. The shortest contact of this kind is 3.69 Å.

3.9. Discussion.

The structure of this salt is very similar to that of the type A acid salts in that it contains a crystallographically symmetrical hydrogen bond. This would explain the infrared spectrum discussed in 3.1.

The N - O single bond length is estimated at 1.44 Å by the method described in page 52. This is in good agreement with the value observed at this stage of the analysis. In 4-nitropyridine-N-oxide (Eichhorn, 1956), the N - O length is 1.26 Å; in N-pyridine oxide hydrochloride (Tsoucaris, 1961), the length is 1.37 Å. Tsoucaris suggests that in N-pyridine oxide hydrochloride there is a strong hydrogen bond between the chlorine and the oxygen, O ... H .... Cl, and quotes structural and infrared evidence in favour of this. In N-α-picoline oxide hemihydrobromide, there are no short contacts between the bromide ion and the polar N - O bond and hence hydrogen bonds between the bromine and the nitrogen or the oxygen are not permissible.

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